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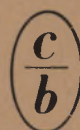
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LITHOLOGY AND MINERAL RESOURCES

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LITHOLOGY AND MINERAL RESOURCES

A translation of *Litologiya i Poleznye Iskopaemye*

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Publication therefore did not occur prior to this date, but must be assumed
to have taken place reasonably soon thereafter.*

In the article, we clarify the basic features associated with the deposition of rare-earth elements and the processes responsible for their distribution within various lithologic types of bottom sediments in the Azov Sea. We establish that the bottom sediments of the coastal area and the halistatic zone are the most enriched. As a result, two peaks of maximum values occur on the granulometric profile: one coincides with fine-grained sands of the beaches, and the other coincides with the clayey muds of the deep-water region. We show the major role of the hydrodynamic regime and the bios in the distribution of rare-earth elements.

The distribution pattern of rare-earth elements in the bottom sediments of the intracontinental seas have gone practically unstudied, despite the fact that they are of tremendous interest for the clarification of a number of questions associated with the geochemistry of sedimentogenesis. The task of our present report is to clarify the principal depositional features and processes responsible for the distribution of rare-earth elements (REEs) in various lithologic types of sediments in the Azov Sea. The geochemistry of the sedimentogenesis in this basin is of special interest by virtue of the uniqueness of the natural depositional environment. Thus, the restricted association with the World Ocean and the large flow of fresh water predetermine a peculiar geochemical regime in contrast to that of other intracontinental seas: low mineralization, heterogeneity of mineralization arising because of the asymmetrical positions of the major water arteries, and a specific ion composition. Moreover, the intracontinental position of the sea results in short- and long-term changes in geochemical parameters under the influence of the climatic conditions which form over the water catchment areas. In essence, the Azov Sea has an isolated existence not directly connected with an ocean, and the geochemical processes which take place within it are characterized by a certain peculiarities.

The data for the report consisted of 92 samples of bottom and beach deposits taken from the water area of the basin. The rare-earth elements were identified by the method of partition paper chromatography at the laboratory in the Department of Geochemistry at Rostov State University.

The total content of rare-earth elements in the sediments of the Azov Sea varies over a wide range: from analytical zero to 0.071%. It is interesting that the bottom sediments of the coastal belt and the halistatic zone (Figs. 1-3) are the most enriched in rare-earth elements. There is a territory situated between these areas which is depleted of rare-earth elements. Two types of maximum values can be detected on the granulometric profile: one coincides with fine-grained beach sands and coarse silts, and the other coincides with deep-water regions (Fig. 4, Table 1). For different areas of the sea, however, the variation in concentrations within these lithologic types (especially the sands) is very great. The variations are primarily a result of two factors: the material composition of the fragmental material being delivered and the intensity of the processes associated with mechanical sorting [20].

The sedimentary material in the Azov Sea arises primarily as a result of the abrasion of rocks composing the shore and bottom and the alluvia of the Don and Kuban rivers [16, 17]. The drift of a significant amount of fine-grained material facilitated the formation of predominantly clayey and fine silty muds over a large portion of the basin. Coarse-grained fractions enter in extremely limited amounts and form the deposits of the littoral zone. The process of mechanical sorting finds expression in the sorting of terrigenous

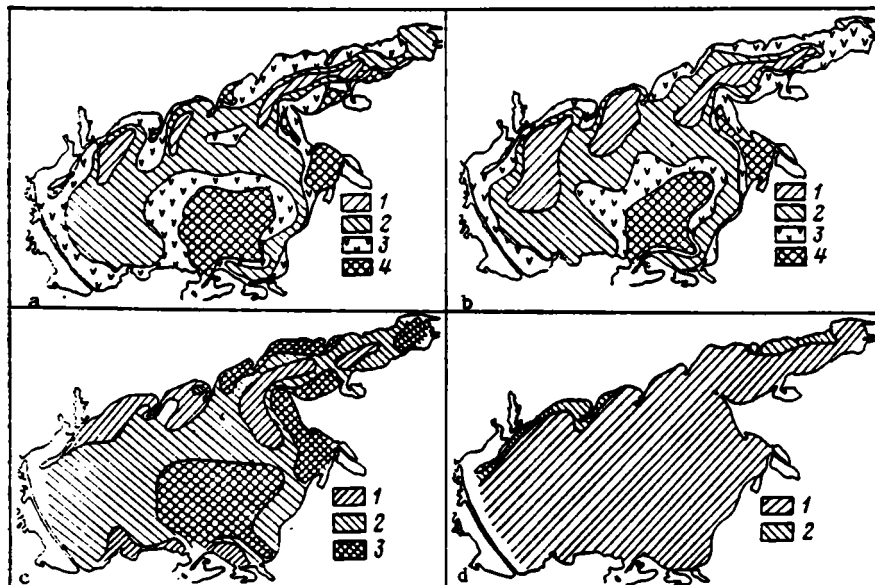


Fig. 1. Distribution of elements in the bottom sediments of the Azov Sea (recalculated for carbonate free-material). a) Rare-earth elements, $10^{-3}\%$: 1) <1 ; 2) 1-5; 3) 5-10; 4) >10 ; b) light lanthanoids, $10^{-3}\%$: 1) <1 ; 2) 1-3; 3) 3-5; 4) <5 ; c) intermediate lanthanoids $10^{-3}\%$: 1) <1 ; 2) 1-2; 3) >2 ; d) heavy lanthanoids, $10^{-5}\%$: 1) <2 ; 2) >2 .

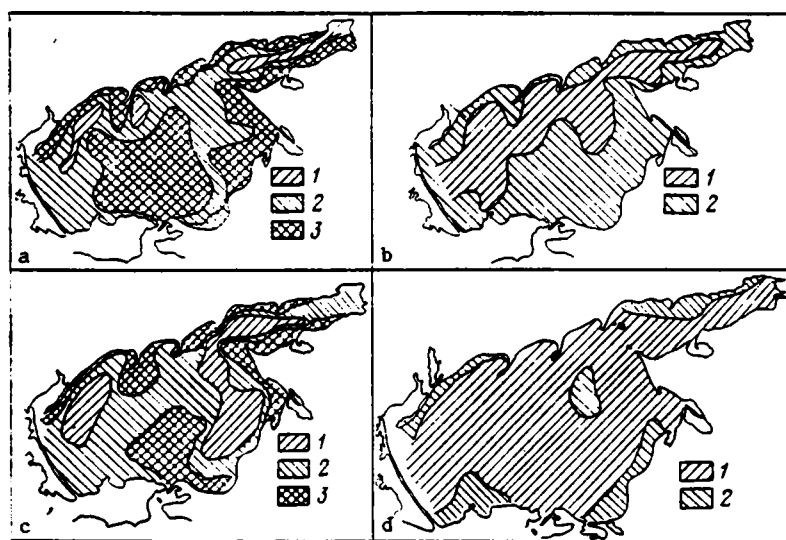


Fig. 2. Distribution of elements in the bottom sediments of the Azov Sea (recalculated for carbonate free-material). a) lanthanum: 1) <0.5 ; 2) 0.5-1.0; 3) >1.0 ; b) series: 1) <1.5 ; 2) >1.5 ; c) praseodymium: 1) <0.25 ; 2) 0.25-0.50; 3) >0.50 ; d) Ce/La: 1) <2 ; 2) >2 .

material not only with respect to size but also with respect to specific gravity. As a result, heavy minerals (garnet, monazite, zircon, etc.) concentrate in individual areas of beach characterized by an active hydrodynamic environment and the delivery of a significant volume material in the sandy fraction during scouring of the coastal rocks. The content of rare-earths in the zircon of the near-shore marine deposits varies from 0.38 to 0.60%; in monazite, it varies from 25.8 to 30.95% [22]. It is not coincidental, therefore, that extreme values of rare-earth elements were found in the beached sediments formed after strong storms. Dark-red placers formed by accumulations of garnet and ilmenite can frequently be found on the surfaces of such deposits. In other areas where the content of heavy minerals is small and the beach sands are primarily represented by quartz, feldspars,

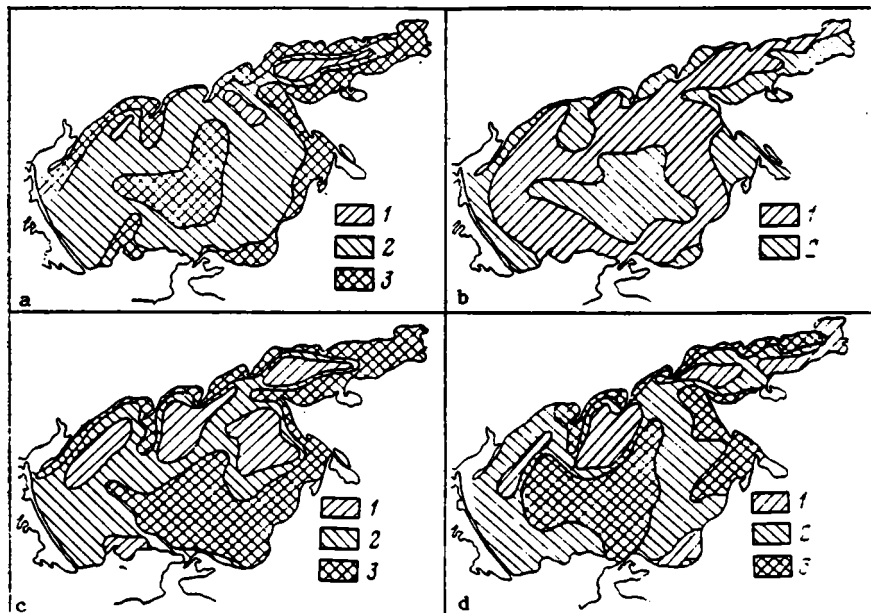


Fig. 3. Distribution of elements in the bottom sediments of the Azov Sea (recalculated for carbonate-free material) $10^{-3}\%$: a) neodymium: 1) <0.5 ; 2) $0.5-1.0$; 3) >1.0 ; b) samarium: 1) <0.5 ; 2) >0.5 ; c) gadolinium: 1) <0.25 ; 2) $0.25-0.50$; 3) >0.50 ; d) dysprosium: 1) 0.25 ; 2) $0.25-0.50$; 3) >0.50 .

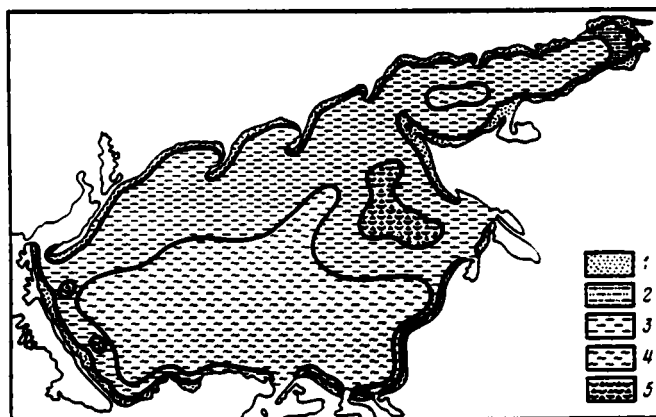


Fig. 4. Distribution of fundamental lithological types of bottom sediments in the Azov Sea: 1) sands; 2) coarse silt; 3) fine silty mud; 4) clayey mud; 5) shell and sand rock.

and rock fragments; the content of rare-earth elements is minimal. Significant variations in concentrations and extreme values of rare-earth elements in the near-shore marine deposits of the Azov Sea are due precisely to the processes associated with mineralogical differentiation.

The material composition of the rocks being eroded, (for the most part the primary source of terrigenous material for the littoral zone) has a vital influence on the content of rare-earth elements on the beaches and subaqueous slope. In the near-shore marine deposits of the southern portion of the sea, the concentration of rare-earth elements is usually lower than in the north. In the region of the Kerchensk Peninsula, the rocks being abraded are predominately limestones and chalks containing limited quantities of minerals in the heavy subfraction and especially mineral varieties with rare-earth elements entering into their compositions. In the northern portion of the sea, the materials which were

TABLE 1 Content of Rare-Earth Elements in Various Lithological Types of Bottom Sediments of the Azov Sea, $10^{-4}\%$ (recalculated for carbonate-free material)

Type of sediment	Sam- ple No.	La	Ce	Pr	La + Pr	Nd	Sm	Gd	Y + Tb	Dy	Nd + Dy	Er	Yb	Er + Ho	$\Sigma P33$	$\Sigma Ce/\Sigma Y$
Clayey muds	21	10,2	17,7	5,0	32,9	12,8	6,3	7,9	5,8	3,8	36,6	0,06	—	0,06	69,6	6,2
Fine silty muds	67	8,3	14,0	3,7	26,0	9,8	4,8	4,3	6,0	2,5	27,4	0,04	0,01	0,05	53,4	5,2
Coarse silts	5	10,9	21,4	3,1	35,4	10,6	2,7	3,0	6,4	3,0	25,7	0,9	0,8	1,7	62,8	5,1
Fine-grained sands	7	26,6	49,4	4,9	80,9	19,1	5,3	3,7	7,0	0,1	35,2	0,03	0,03	0,12	116,2	15,1
Omitting anomalous values	6	2,5	4,1	1,5	8,1	2,4	0,2	0,2	0,3	0,1	3,2	0,03	0,05	0,08	11,4	22,7
Medium-grained sands	7	6,9	11,0	1,1	19,8	5,0	1,8	1,6	2,1	1,1	11,6	—	—	—	31,4	8,8
Shell and sand rock	5	22,4	22,7	5,2	50,4	17,9	5,9	7,8	11,3	2,2	45,1	—	—	—	95,5	6,1

TABLE 2 Complete Rare-Earth Distribution Breakdown for Recent Sediments and Sedimentary Rocks

Sediments, rocks	Rare-earth elements, % (of total)											$\Sigma Ce/\Sigma Y$	Source
	La	Ce	Pr	Nd	Sm	Eu + Gd	Tb + Y	Dy	Ho	Er	Yb		
Clays	17,8	35,1	4,7	16,8	3,9	4,1	13,2	2,0	—	1,4	1,1	4,7	[11]
Russian Platform*	20,5	40,4	5,4	19,4	4,5	4,7	—	2,3	—	1,6	1,3	—	
Clayey muds for Azov Sea	14,7	25,4	7,2	18,4	9,1	11,4	8,3	5,4	—	0,1	—	6,2	Our data
	16,0	27,7	7,8	20,1	10,0	12,4	—	5,9	—	0,1	—	—	
Muds	17,9	35,6	4,6	17,2	3,2	3,2	15,0	1,5	0,2	0,8	0,6	4,5	[14]
Black Sea	21,0	41,9	5,4	20,2	3,8	3,8	—	1,8	0,2	1,0	0,7	—	
Clayey muds of Pacific	14,3	32,1	4,1	16,4	3,0	4,0	22,0	0,9	0,3	1,4	1,3	2,9	[14]
Ocean (red clays)	18,3	41,1	5,2	21,5	3,8	5,1	—	1,1	0,4	1,8	1,6	—	

Explanation. First value: sum of rare-earth elements, including Y; second: without Y.

*Data compiled by L. S. Fomin and I. I. Volkov [14].

eroded were Neogene and Paleogene sands and clays of alluvial and marine origin (the accumulation of these materials was connected with the breakdown of the crystalline rocks of the Ukrainian shield). The possibility of forming beach deposits with elevated quantities of garnet, monazite, zircon, and other minerals containing rare-earths was assured because of the supply of terrigenous material to the near-shore zone resulting from the abrasion of these rocks) especially the sands) [17]. The concentration of REEs is usually significantly lower in areas where Scythian clays and loess-type loams were eroded.

Thus, the combination of an intensive hydrodynamic regime and a supply of terrigenous material characterized by an elevated concentration of minerals in the heavy-mineral fraction led to a local enrichment of near-shore marine deposits with rare-earth elements, and, as a consequence, to maximum REE values identified on the beaches of intensively eroded coasts composed of terrigenous rocks. The sands and coarse silts of the coastal zones of other areas where hydrodynamic conditions are tranquil and impoverished with respect to rare-earth elements.

The second maximum in elevated concentrations of rare-earth elements coincides with clayey muds of the halistatic zone of the Azov Sea. In contrast to the near-shore marine deposits, the rare-earth elements here are distributed relatively uniformly over the area of the basin. Only in an area adjacent to the Kerchensk Strait does the content of rare-earth elements increase significantly. The analogous distributions of organic carbon, amorphous silica, and pelitic fractions have led to the idea that the bios, and, most importantly, the phytoplankton and the processes of sorptive extraction associated with their pelitic pellets, play definite roles in the concentration of rare-earth elements in the fine-grained deposits. The actuality of a similar enrichment of the bottom sediments of the halistase is also confirmed by the increase in the fraction of intermediate lanthanoids (see Table 1) incorporated predominately into the sorption complex of a marine suspension [1] and by the elevated concentration in shell and rock sands (in a recalculation for carbonate-free material), especially in an area located near the Eisk Peninsula (see Fig. 1c).

The existing published information on the sorption of rare-earth elements by clay minerals is fairly contradictory, but all the information indicates that the sorption is of a selective character. According to the data of Shcherbin [23], clay minerals absorb light rare-earth elements more easily than heavy ones. According to experiments, hydromica and kaolinite accumulate lanthanum to a lesser degree than do dysprosium and gadolinium [24]. The differential character of the absorption of rare-earth elements by clay minerals was pointed out by Balashov and Girin [2], who were of the opinion that light REEs were maximally accumulated by kaolinite, intermediate REEs by hydromica, and heavy REEs by montmorillonite. It is undoubtedly the case that the intensity of the sorption by clay minerals and their selective capability were determined not only by mineral composition but also by the natural conditions associated with the sedimentogenesis. Keep in mind that the compositional mix of clay minerals in the sediments of the Azov Sea varies negligibly over the water area (clay minerals are principally represented by hydromica with an insignificant admixture of chloite, kaolinite, and montmorillonite); their roles in the fractioning of the REEs are apparently minor [19], but the part played by the finely pelitic fraction of the accumulations or rare-earth elements in the bottom sediments is significant. It is not accidental, therefore, that a definite connection exists between the amount of fine-grained material and the concentrations of rare-earth elements in the sediments of the Azov Sea. The data obtained indicates enrichments of the intermediate lanthanoids are characteristic of the clay deposits of the basin; these are; neodymium, samarium, gadolinium, dysprosium, and also praseodymium (see Table 1). Data from experimental investigations also indicate a preferential sorption of intermediate and heavy lanthanoids in comparison with light lanthanoids in comparison with light lanthanoids (for sorption by clay minerals) [24]. The information presented indicates that the intermediate lanthanoids are more actively sorbed and more simply bonded by the subcolloidal fraction than by the light fraction. The saline regime of the sea apparently exerts a definite influence upon the intensity of the sorption processes. Therefore, the clayey muds of the prestrait area, characterized by an elevated mineralization of the water layer as a result of a constant supply of Black-Sea waters, are the most enriched with rare-earth elements (see Fig. 1c).

Concentration of rare-earth elements in the fine-grained sediments occurs also as a result of biochemical processes. Algae actively consume, and their remains intensively absorb rare-earth elements. As investigations have demonstrated, the average content of lanthanum in phytoplankton of a primarily diatomic composition reaches 0.0025%, the average

content of yttrium reaches 0.002% and that of ytterbium reaches 0.001%. This is significantly higher than the concentrations of these elements in clayey muds. Burial of algal remains is usually accompanied by an enrichment of the bottom sediments. Breakdown of these bottom sediments is one of the primary sources of rare-earth elements during diagenesis.

In addition to biological assimilation and accumulation in tissues, a portion of the elements are actively sorbed on the surface of the plankton and its detritus. The experiments mentioned confirm the significant role of sorption of cerium from solution by biogenic detritus [4]. More than half of the dissolved element was extracted from the sea water during the process of an experiment.

The bottom sediments of the Azov Sea are characterized by a negligible amount or by a complete absence of heavy rare-earth elements. Such elements occur in local areas, gravitating primarily toward near-shore marine and beach deposits and forming maximum accumulations in the coarse silts of the subaqueous slope, where a heavy subfraction enriched in zircon is common. As a rule, rare-earth elements do not occur in fine silty muds and clayey muds, shell and rock sands, and the medium-grained sands of heavy lanthanoids (see Fig. 1d). Such a distinction with respect to the composition features associated with REEs indicates the existence of an intensive mineralogical differentiation and a coincidence of heavy lanthanoids with zircon, monazite, and garnet. Snyukov et al. [22] has indicated a significant content of heavy lanthanoids in Azovian monazites.

The distribution patterns of rare-earth elements described in the bottom sediments of the Azov Sea are somewhat modified in regions of biogenic carbonate sediments. It is usually assumed that the carbonate material is of the nature of a diluting agent, decreasing the content of chemical elements in marine sediments. As Ostroumov [8] and Balashov et al. [3] showed, the carbonate deposits and rocks are significantly impoverished of rare-earth elements in comparison with clayey muds and silts. There is another point of view according to which the biogenic carbonate component is an additional source of REEs in oceanic sediments [6, 7]. Apparently, this conclusion holds for the geochemistry of rare-earth elements in the Azov Sea. As investigations have shown, the content of rare-earth elements is significantly lower in shell and rock sands (in native sediment) than in clayey muds (0.0026 and 0.0042% respectively). However, when making recalculations for carbonate material, it turns out that the average content of rare-earth elements in carbonate sediments is 1.5 times higher than in terrigenous sediments (see Table 1). All of this indicates an active role for benthic organisms in the distribution of rare-earth elements in the bottom sediments of the Azov Sea. The REEs of shell and rock sands differ with respect to composition from the REEs terrigenous deposits in the relative enrichments of lanthanum, yttrium and the terbium and the impoverishment of zircon. This is apparently a characteristic feature of the REE compositional mix in the marine sediments of the arid zone. A deficit of zircon in arid carbonate rocks was pointed out by Ronov, Balashov, and Migdisov [11, 12] when they discussed the geochemistry of rare-earth elements in the sedimentary cycle.

The biogenic components affect not only the total content but also the compositional mix of rare-earth elements. This effect is realized both by the burial of rare-earth elements together with products of the life activities of pelecypod mollusks. The pellets deposited on the bottom are enriched with organic matter in comparison to the sediments of the substrate on which the mollusks live [21]. Undoubtedly, this intensifies absorption processes which also facilitate the enrichment of the bottom sediments.

A predominance of intermediate lanthanoids in fine-grained varieties (clayey and fine silted muds) is a characteristic feature of the mixture of the rare-earth elements in the sediments of the Azov Sea. The coincidence of intermediate lanthanoids with marine facies formed within various climatic zones was noted by Balasov [1]. In his opinion, the prevalence of intermediate lanthanoids in marine deposits was caused by an intensification of the processes of chemical separation of rare-earth elements, as a consequence of which, the overwhelming mass of rare-earth elements entering into the weathering cycle are concentrated in the fine-grained granulometric fractions. A similar conclusion was apparently reached on the basis of investigations concerning the distribution of REEs in the fine-grained sediments of the Azov Sea.

As is evident from Table 1, light lanthanoids predominate in the fine-grained varieties of bottom sediments (coarse silts and sands). The formation of coarse silts and sands oc-

curred primarily as a result of the abrasion of the rocks composing the shore, i.e., sedimentary material arrives to the shore zone under the action of physical processes and, at the present time, is not subjected to intensive chemical weathering. As a consequence, rare-earth elements are linked to such minerals as garnet, amphiboles, zircon, and monazite.

In the opinion of Balashov [1], the relative content of intermediate lanthanoids and, to a lesser degree, heavy lanthanoids, increases for the transition from continental facies to marine facies, i.e., light lanthanoids predominate in continental deposits and intermediate lanthanoids predominate in marine deposits. Actually, intermediate lanthanoids play the leading role in the compositional mix of rare-earth elements in red clays and other lithological types of oceanic sediments [6, 13]. From the material presented, it is evident that features natural to both groups of facies characterized above are combined in the distribution of REEs in the bottom sediments of the Azov Sea. This is manifest in the predominance of intermediate lanthanoids in the fine-grained sediments and the predominance of intermediate lanthanoids in coarse silts and sands. The causes which produced the similar distributions of REEs in the bottom sediments of the basin are fairly evident. They are intracontinental position, small dimensions, and shallow water. It is precisely because of these natural factors that the near-shore marine sands and coarse silts carry indications of a compositional mix of REEs which is characteristic of the products of coastal abrasion (loess-type loams) and alluvial material, i.e., characteristic of continental facies. The marine conditions for the sedimentogenesis are manifest in the coincidence of intermediate lanthanoids with fine silty muds. Thus, one can conclude that features intrinsic to both the continental and marine facies are characteristic of the distribution of rare-earth elements in sediments of the Azov Sea. One should not lose sight of the fact that the similar distribution and compositional mix of rare-earth elements agrees beautifully with modern hypotheses concerning the geochemical behavior of REEs during the chemical weathering of rocks. According to the suggestions of Balashov [1], the primary result of the separation of rare-earth elements during weathering is the relative enrichment of the fragmental material with light lanthanoids and the relative enrichment of a transformed complex (clay minerals) with intermediate lanthanoids.

One of the peculiarities in the compositional mix and distribution of rare-earth elements in the bottom sediments of the Azov Sea is the high $\Sigma Ce/\Sigma Y$ value. The range of variation for this coefficient is from 5.1 in coarse silts to 22.7 in fine-grained sands, i.e., the overall character of the change in the compositional mix of REEs in the sediments of the basin tends toward the side of enrichment of the sediments with the elements of the ceric subgroup and a sharp decrease in the content of yttrium (see Table 1.) The value of $\Sigma Ce/\Sigma Y$ common in the sedimentary rocks of modern seas and oceanic sediments is within range of 2 to 4 and only reaches values of 7.1 in the continental humid deposits of the Russian Platform [1, 6, 13]. Keeping in mind that substantial transformation of the compositional mix of REEs does not occur in the basin itself and that the distribution of REEs with respect to fundamental lithologic types of bottom sediments is determined primarily by mechanical workings, the increased $\Sigma Ce/\Sigma Y$ values in comparison with those for sedimentary rocks and oceanic sediments should be attributable to specifics associated with the chemical composition of the rocks of the catchment systems.

As is well known, the dominant role of the products of the abrasion of the shores and bottom in the supply of terrigenous material is a characteristic feature of the sedimentational balance of the Azov Sea [16, 17]. Determinations of the absolute ages of the zircon and monazite (the principal mineral-concentrators of rare-earth elements) collected from the beach deposits indicate that the ages are Precambrian [22]. All of this indicates that the terrigenous minerals, and, consequentially, the fragmental material, gradually underwent intensive chemical weathering and reworking which predetermined a partial segregation of rare-earth elements. Besides the evolution of the compositional mix of REEs during weathering, the chemical compositions of the original rocks (Precambrian granites) have no less importance. The Precambrian granites of the Preazovsk crystalline massif are characterized by a ceric compositional mix of rare-earth elements. The average content of elements of the ceric subgroup vary from 93.9 to 96.8%. This is significantly higher than in sedimentary rocks [1, 10]. Only a ceric composition of the REEs in the granites and their segregation during chemical weathering and mechanical sorting can explain the high $\Sigma Ce/\Sigma Y$ values in the bottom sediments of the Azov Sea. A report [22] based on a study of the isotopic ages

of the minerals indicated a leading role for the Preazovsk crystalline massif as a source of the most important ore minerals in foreshore-marine deposits, not only for Northern Preazov'ya but also for the entire water area of the Azov Sea.

When comparing the $\Sigma\text{Ce}/\Sigma\text{Y}$ values in the Precambrian granites and in various lithological types of sediments of the basin, the following fact stands out. The coefficient increases in fine-grained sands. Apparently, fractionation of the REEs takes place during weathering of the granites. As was demonstrated by Podporinov and Burkov [9], the clayey fractions of the weathering crust are somewhat enriched in Y with respect to group composition and practically identical with respect to ΣLa in comparison with bulk samples.

One should not neglect the partial supply of rare-earth elements from the constant flow of the Don and Kuban rivers. It is widely known that the terrigenous material of these rivers forms primarily as a result of scouring of sedimentary rocks with small $\Sigma\text{Ce}/\Sigma\text{Y}$ values. Thus, the $\Sigma\text{Ce}/\Sigma\text{Y}$ value does not exceed 3.41 for the Russian Platform, 4.21 for the Skifsk Platform, and 3.66 for the intermontaine troughs of the Lesser Caucasus [12]. Undoubtedly, the low values of $\Sigma\text{Ce}/\Sigma\text{Y}$ in these rocks the REE composition of alluvium and, consequently, the bottom sediments of the Azov Sea. This is expressed in the decreased concentration of elements in the ceric subgroup and in increased concentration of elements in the yttric subgroup. The influence of the various sources of supply of terrigenous material upon the distribution of dysprosium stands is especially marked. As is evident in Fig. 3d, the maximum concentration of the element is noted in the sediments of near-shore shoals in the northern portion of the Azov Sea, thus indicating delivery along with fragmental material during the scouring of coastal rocks. At the same time, the content of dysprosium is minimal in the bottom sediments in the fore-delta regions of the Don and Kuban rivers. Apparently, the alluvia of these rivers are impoverished of this element.

Thus, the analysis of the $\Sigma\text{Ce}/\Sigma\text{Y}$ values in the bottom sediments of the Azov Sea indicate that the composition of rare-earth elements determined to a significant degree by the material composition of the matrix rocks. The analysis also indicates that the composition of rare-earth elements is a beautiful indicator of the intensity of the process of chemical weathering upon catchment areas. Despite multiple reworkings of the terrigenous material, the sediments of the basin inherit ratios of rare-earth elements characteristic of the granites and granite-gneisses of the Asovsk crystalline massif. Drifts from the Don and Kuban rivers introduce certain correctives to the compositional mix of the REEs in the bottom sediments.

When comparing the $\Sigma\text{Ce}/\Sigma\text{Y}$ values for the bottom sediments of the Azov and Black seas and the red clays of the Pacific Ocean, one can see a regular decrease in the values of this coefficient fairly clearly; this indicates an enrichment of the red clays of the Pacific Ocean with yttric earths (Table 2). The value of $\Sigma\text{Ce}/\Sigma\text{Y}$ is 6.2 in the pelagic sediments of the Azov Sea and 4.7 in the Black Sea, but it is only 2.9 overall in the Pacific Ocean, i.e., a decrease in the value of this ratio is observed with increasing dimensions of the basin. As was shown by Balashov [1], yttrium and heavy lanthanoids actively pass into solution during the formation of weathering crust. During the stage of yttrium sedimentogenesis, yttrium has a higher geochemical mobility than lanthanoids despite the fact that the chemical properties of yttrium are similar to those of lanthanoids. Because of these qualities, yttrium accumulates in the pelagic sediments of the ocean to a great extent [14].

The rare-earth elements fall into the following order with respect to migrational capability during the sedimentation cycle as expressed by distribution in bottom sediments and coincidence with definite lithological types:

2,0	2,1	3,6	3,8	4,8	5,7	6,3	8,8
Ce	La	Nd	Pr	Y + Tb	Sm	Dy	Gd

The values obtained indicate a regular increase in the mobilities of the elements in the cerium-gadolinium series. It is interesting that the light lanthanoids (cerium and lanthanum), in which the coefficient of the pelagic shift is approximately 2, are located on the left side of the series. The coefficients for the intermediate lanthanoids increase and reach those of dysprosium and gadolinium (6.3 and 8.8, respectively). Judging from the high values of the coefficient of migrational capability, one can conclude that the elements under investigation are characterized by a significant differentiation of concentrations. As was conclusively shown in a report [12], the high degree of differentiation in the con-

tent of REEs in terrigenous rocks was reached as a result of multiple reworkings of the sedimentary material. This conclusion is valid for the geochemistry of rare-earth elements in the Azov Sea. Prior to entry into the basin, the original sedimentary matter, minimal over the course of four preceding orogenic cycles (the Baikal, Caledonian, Hercynian, and Alpine), underwent intensive reworking and became fairly differentiated during the earlier stages in the evolution of this territory [12].

Despite similar coefficients of pelagic shift in concentration, the geochemical behaviors of lanthanum and cerium are far from identical. As is evident from Fig. 2a, b, the maximal values of lanthanum tend to be for shallow-water and pelagic sediments. In the first case, the increase in content is the result of accumulation of mineral-carriers of REEs in the northern and eastern shoals; in the second case, the increase is due to intensive accumulation of the subcolloidal fraction and organic matter [5]. The distribution of cerium concentrations in the sediments of the Azov Sea are relatively uniform over a large portion of the water area. Minimal quantities coincide with fine silty muds (see Fig. 2b). The diagram of the distribution of Ce/La values in the bottom sediments of the basin indicate the different geochemical behaviors of the elements (see Fig. 2d). It should be noted that this ratio is, as a rule, greater than unity for the sediments of the Azov Sea; maximum values are found within the northern shals. These are the regions from the Arabatsk spit to the sandbars of the Pbitochnoi and Taganrogskii bays. An area where the Ce/La value is less than 2 is located between them. Keeping in mind that the source of supply of sedimentary material here is one and the same (products of coastal abrasion), it is extremely difficult to explain so substantial a difference in the chemical composition of the REEs in the shallow-water sediments. The primary reason for the similar anomaly is hidden in the different chemical compositions of the mineral-carriers of the REEs and the sources of supply of terrigenous minerals to the northern shore. Differences in the typomorphic indicators and the chemical compositions of ilmenite, zircon, and monazite are indications of this [22].

The Ce/La values in the sediments of the fore-delta region of the Kuban River are fairly high, despite the fact that this indicator is within a range of 1.6-1.7 for the fluvial suspension [7]. Probably, the fragmental material delivered to the sea shore with the river flow, having underwent substantial mechanical differentiation, facilitated the enrichment of the bottom sediments with cerium and facilitated an impoverishment with respect to lanthanum.

Data on the ratio of cerium and lanthanum in biogenic carbonate sediments can serve as evidence of the separation of these elements during the stage of sedimentogenesis. This coefficient is, on an average, approximately equal to unity, with the Ce/La value significantly greater than unity in all of the varieties of terrigenous deposits, as indicated above. Apparently, biogenic carbonate and organic material play a significant role as carriers of lanthanum. At the same time, mollusks consume small quantities; this is what leads to such low Ce/La values.

Thus, rare-earth elements are delivered to the sediments of the Azov Sea primarily along with terrigenous material. The hydrodynamic regime thus plays a leading role in their distribution. An enrichment of the foreshore-marine and shallow-water deposits, especially with lanthanum and garnet, takes place as a result of mechanical sorting [15]. The other fraction of rare-earth elements enter into bottom sediments in a composition of clay minerals which fixes high concentrations of lanthanoids in the clayey muds.

The influence of the bios is clearly manifest in the family of rare-earth elements, even at the stage of sedimentogenesis. Their accumulations in phytoplankton lead to an increase in concentration within clayey muds characterized by maximum values of organic matter associated with amorphous silica. Benthic organisms introduce significant correctives during the course of the mechanical distribution of the REEs [18]. As a result of their influence, biogenic carbonate sediments turn out to be the sediments most enriched. The increase in the concentration of intermediate lanthanoids with increasing amounts of the pelitic fractions is a characteristic feature of the chemical composition of the rare-earth elements of the bottom sediments of the Azov Sea; an almost complete absence of heavy lanthanoids is also characteristic.

LITERATURE CITED

1. Yu. A. Balashov, *Geochemistry of Rare-Earth Elements* [in Russian], Izd. Akad. Nauk SSSR, Moscow (1976).
2. Yu. A. Balashov and Yu. P. Girin, "The reserve of mobile rare-earth elements in sedimentary rocks," *Geochemistry*, No. 7, 207-216 (1969).
3. Yu. A. Balashov, A. B. Ronov, A. A. Migdisov, and N. B. Turanskaya, "The influence of climatic and facies conditions upon the segregation of rare-earth elements in the sedimentation process," *Geochemistry*, No. 10, 995-1014 (1964).
4. *The Biochemistry of the Ocean* [in Russian], Nauka, Moscow (1983).
5. V. R. Volobuev, "Content of elements in the zone of plant life (analysis of the problem from the point of view of energetics)," *Izv. Akad. Nauk SSSR, Ser. Biol.*, No. 5, 656-662 (1968).
6. I. I. Volkov and L. S. Fomina, "Rare-earth elements in the sediments and manganese concretions of the ocean," *Litol. Polezn. Iskop.*, No. 3, 66-85 (1967).
7. A. P. Lisitsyn, E. G. Gurvich, V. N. Lukashin, et al., *Geochemistry of Elements - Hydrolizers* [in Russian], Nauka, Moscow (1980).
8. É. A. Ostroumov, "Rare earths in deep-water deposits of the Black Sea," *Dokl. Akad. Nauk SSSR*, 91, No. 5, 1175-1178 (1953).
9. E. K. Podporina and V. V. Burkov, "Rare-earth elements in the process of weathering biotite pyroxenites," *Litol. Polezn. Iskop.*, No. 4, 38-53 (1977).
10. K. I. Rozanov and D. A. Mineev, "Geochemical characterization of the Precambrian granitoids of Preazov'ya," *Geochemistry*, No. 2, 238-249 (1973).
11. A. B. Ronov, Yu. A. Balashov, and A. A. Migdisov, "Geochemistry of rare-earth elements in the sedimentary cycle," *Geochemistry*, No. 1, 3-19 (1967).
12. A. B. Ronov, Yu. A. Balashov, Yu. P. Girin, et al., "Distribution pattern of rare-earth elements in the sedimentary mantle and in the Earth's crust," *Geochemistry*, No. 12, 1483-1514 (1972).
13. N. M. Strakhov, *Problems of the Geochemistry of Modern Oceanic Lithogenesis* [in Russian], Nauka, Moscow (1976).
14. L. S. Fomina and I. I. Volkov, "Rare-earth elements in the sediments of the Black Sea," *Litol. Polezn. Iskop.*, No. 148-160 (1970).
15. V. N. Kholodov, "The types of concentrations of rare elements in sedimentary rocks and some general problems in the theory of ore formation," in: *The State and Problems of Soviet Lithology* [in Russian], Vol. 2, Nauka, Moscow (1970), pp. 130-141.
16. Yu. P. Khrustalev and F. A. Shcherbakov, "The balance of sedimentary material in the Azov Sea," *Okeanologiya*, 8, No. 3, 452-461 (1968).
17. Yu. P. Khrustalev and F. A. Shcherbakov, "Late Quarternary deposits of the Azov Sea and the conditions of the accumulation," *Rostov State Univ., Rostov-on-Don* (1974).
18. Yu. P. Khrustalev, "Trophic geochemistry and its problems," in: *The Biochemistry of the Oceans* [in Russian] (Text from an All-Union Conference), Moscow (1984).
19. Yu. P. Khrustalev and G. K. Khrustaleva, "Toward a mineralogy of the highly dispersed portion of the bottom sediments of the Azov Sea," *Izv. Severo-Kavkaz Naukhn. Tsentra Vyssh Shkoly, Estestv. Nauki.*, No. 4, pp. 98-100 (1976).
20. Yu. P. Khrustalev and G. I. Lebed'ko, "Rare-earth elements in the bottom sediments of the Azov Sea," *Geokimiya*, No. 5, pp. 797-800 (1981).
21. Yu. P. Khrustalev, I. A. Mirzoyan, and M. Ya. Nekrasov, "Sedimentary role of zoobenthic filtrates based on the example of the Azov Sea," *Litol. i. Polezn. Iskop.*, No. 6, 84-96 (1984).
22. E. F. Shnyukov, G. N. Orlovskii, V. P. Usenko, et al., *Geology of the Asov Sea* [in Russian], Nauk. Dumka, Kiev (1974).
23. V. B. Shcherbina, "Geochemical basis for classifying the rare-earth elements," in: *Rare-earth Elements and Their Deposits. Geology of Rare-earth Deposits*, No. 3, Gosgeoltekhizdat, Moscow (1959), pp. 1-24.
24. P. Aagard, "Rare-earth elements adsorption on clay minerals," *Bull. Groupe franc argilles*, 26, 2, 193-199 (1974).

STRUCTURE OF UNDERWATER ALLUVIAL CONES, USING LAKE BAIKAL AS AN EXAMPLE

V. G. Nikolaev

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The structure of the sedimentary cover of portions of the terrigenous alluvial material entering Lake Baikal from the Selenga and Upper Angara rivers is examined. In the first case, an underwater alluvial cone formed, while in the second case a sedimentation body of a lateral infilling complex formed. The position of the lower Pleistocene trough which played the role of the main channel for the alluvial cone of the Selenga River is established. It is compared with other alluvial cones (the Mississippi and Danube rivers, etc.). Conclusions are drawn on several causes leading to the formation of different forms of sedimentational bodies.

The Selenga River is the largest supplier of sedimentary material to Lake Baikal. Its delta, including the underwater portion, is approximately 40 km in length and 60 km in width. Morphological and geological descriptions of the delta are presented in many articles [3, 6, 8, etc.]. Sediments carried out by the Selenga River fill the Selenginsk depression. The thickness of these sediments reaches nearly 5 km [3]. They are represented exclusively by terrigenous types of sediments and rocks. The internal structure of the underwater extent of the Selenga River delta is successfully determined only with the aid of seismic sections. Seismic profiling was conducted by various methods [1, 9].

The underwater extent of the Selenga River delta extends over 10-20 km, forming the Lake Baikal accumulative shelf (Fig. 1). Then the floor surface experiences rather abrupt subsidence into the side of the Southern and Central trough to depths of 900-1000 m. This segment, from 10 to 20 km in width, relates to the continental slope. It is absent in the region of the Bugul'deisk connecting bridge. A sharp transition to the abyssal trough occurs at the lower part of the continental slope, where the surface of the floor is practically horizontal.

Within the limits of the underwater extent of the Selenga River delta, seismic profiles illuminate the section of sedimentary cover only to a depth of 1.0-1.5 km, and reliable reflections from acoustical basement were not obtained [9]. The layers have a general dip in the direction of the deepwater trough. In the central part (Fig. 2), several separate sedimentary bodies are distinguished in the section, some of which are tapered in both directions. Their dimensions (transverse to the continental slope) reach a few kilometers, and their thickness varies from tens to 100-200 m. Sizes of the bodies along the strike of the shelf edge are poorly established, but they hardly exceed a few tens of kilometers; it is difficult to detect similar forms since only 20-30 km north of the cited section.

Layers inside the bodies are positioned very diversely. In one case they lean toward the bottom of the body, both on the periphery and in the central part of the body. In other cases, on small portions, truncation of discrete layers by the upper boundary of the body is observed. Complete parallelism of layers on the upper and lower boundaries of the bodies is also recorded.

Two sedimentary bodies are distinguished by internal structure: one is positioned in the eastern part of the seismic profile, on the shelf; the other forms the upper part of the section of sedimentary cover of the Southern trough. In it, the layers are on the whole parallel to the floor surfaces, which is apparently the upper boundary of body, and they are inclined against its lower boundary by the latter's uplifting. On the north, the lower boundary and the overlying layers preserve a subhorizontal position and are cut by a fault

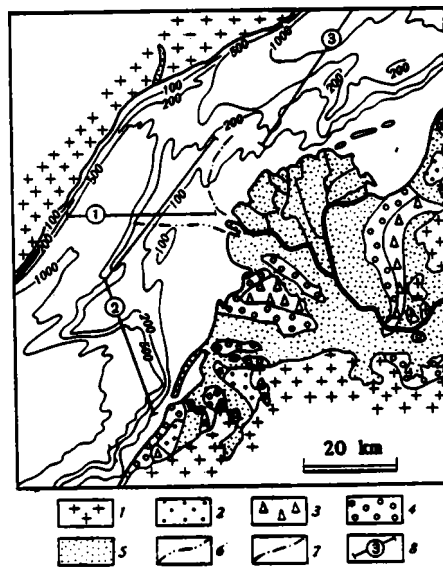


Fig. 1. Geological map of the region of the Selenga River delta region: 1) Pre-Neogene rocks; 2) Pliocene (Anosovsk suite); 3) Eo-Pleistocene-lower Pleistocene; 4) middle-upper Pleistocene; 5) upper Pleistocene-Holocene; 6) Paleo-channel of the Selenga River; 7) main recent underwater channel of the Selenga River; 8) lines of seismic profiles, presented in Figs. 2-4.

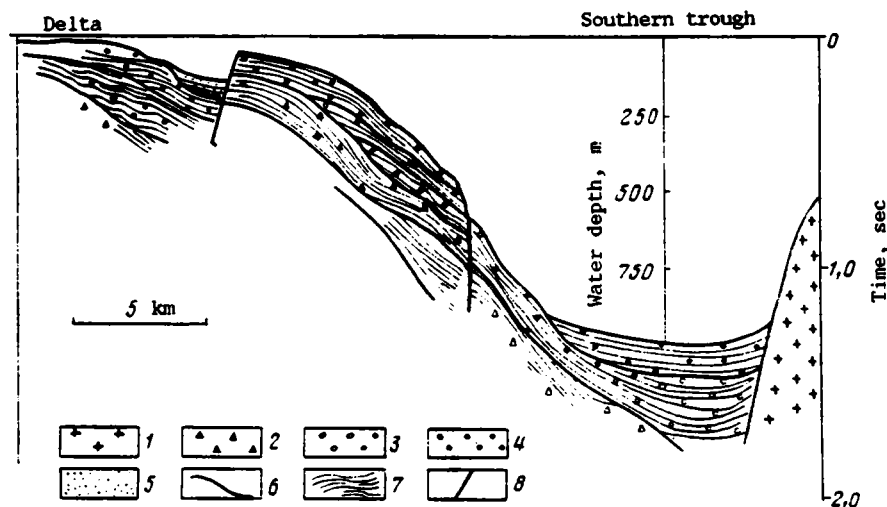


Fig. 2. Seismic profile 1 across the Selenga River delta (see Fig. 1): 1) Pre-Neogene basement; 2) upper Pliocene; 3) Eo-Pleistocene-lower Pleistocene; 4) lower-middle Pleistocene; 5) upper Pleistocene-Holocene; 6) boundary of geological bodies (seismocomplexes); 7) layers inside bodies (in-phase axes); 8) fractures.

plain. As a result of bottom test core sampling, the age of the considered body is estimated at lower-middle Pleistocene. Negative forms of relief are observed on the shelf. These are filled in by supposedly upper Pleistocene-Holocene layered sediments up to 100 m in thickness. They are inclined against the underlying formations (analogously to correlations in the Southern trough).

Deposits of the lower-middle Pleistocene are almost universally absent in the transition to the abyssal trough, at depths of approximately 700-900 m. Rocks of Eo-pleistocene-lower Pleistocene occur here at the surface of the floor.

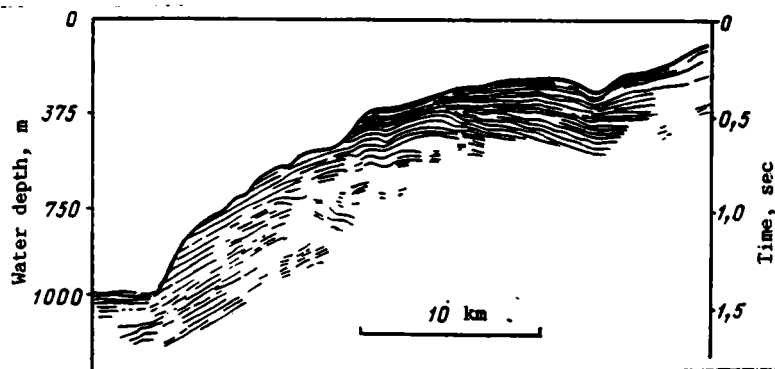


Fig. 3. Seismic profile 3 across the Selenga River delta, illustrating the strong shearing of layers at the base of the continental slope, and the presence of inclining bodies (see Fig. 1).

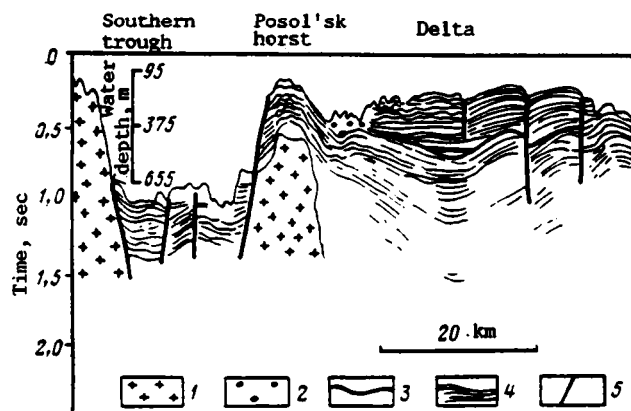


Fig. 4. Seismic profile 2 transverse to the Selenga River delta (see Fig. 1). 1) Pre-Neogene basement; 2) slump body; 3) boundary of seismic-complexes (paleosurface); 4) layers inside complexes (in-phase axes); 5) fractures.

The height of the sheared portions varies from 30 to 300 m (Fig. 3). The value of the slope of the floor surface in the shearing zone does not depend on the dip angle of the sheared layers. It reaches a few degrees, often 5-6°. In addition, cases are observed when the layers are curved parallel to the surface of the lower part of the continental slope, and its dip is flattened out to one-two degrees. Seismic profile 2 (Fig. 4) occurs transverse the extent of the Selenga River delta. The South-Baikal trough is located in its southern part, while in the north it intersects lenticular bodies. Two complexes are established in the profile. The lower seismocomplex, dated as Eo-Pleistocene-lower Pleistocene, has apparent thickness of nearly 1000 m. Only its upper part is characterized. A rather narrow valley, framed on the edges by small protuberances is recognized on the sediment surface of this complex. They valley is cut to a depth reaching nearly 200 m. They layers inside the lower complex repeat the profile of its cover. The upper seismocomplex presents itself as a lens of deposits tapering to the north and south. Their maximum thickness reaches approximately 350-400 m. The bottom layers of the upper complex fills in depressions in the paleo-relief of the lower complex, the layers are on the whole curved in relation to the cover. Gradual thinning of individual layers of the upper complex occurs towards the edges of the lens. Chaotic traces are observed on the southern edge of the lens close to the surface of the floor. This is interpreted as reflection from slump bodies with disturbed layered structure.

A series of fractures with subvertical dip of their planes is traced on the north of the lens' end. They are expressed in the floor's relief by small terraces. The amplitude of the fractures is not great, and it varies from a few tens to hundreds of meters. The limbs are lowered within the limits of the continental slope, facing toward the abyssal trough. The reverse picture is sometimes observed on the shelf, when a block adjacent to the shore line is lowered (Fig. 2). The majority of small amplitude fractures, as a rule, changes their strikes as if outlining the shore line. In this they are distinguished from the large amplitude fractures, which have a southwest-northeast strike and are positioned parallel to the edges of the Baikal depression.

The considered series of lenticular bodies of relatively small thickness represents the underwater alluvial cone of the Selenga River. They are most distinctly seen in the upper part of the section of sedimentary cover. The lenticular bodies may be compared with blades of underwater deltas, whose position varies dependent on the position of the primary river bed channel. Narrow tectonic hollows of early Pleistocene age are established in a series of seismic profiles. During the early-middle Pleistocene they played the role of underwater channels, directed to the side of the South-Baikal trough. The main recent underwater channel has an analogous tectonic genesis. It is directed to the side of the Central-Baikal trough. The strike of the underwater channels determines the primary direction of material transfer. In agreement with this, in the early-middle Pleistocene it went to the south, while in the late Pleistocene-Holocene it went to the west. This is also confirmed by analysis of the sediment thickness in different structures [11].

In time, the lenticular bodies successively form the continental slope, which migrates to the side of the deep water trough. The shore line advances in this direction on account of the delta's growth. If one extrapolates modern delta growth rates (10-12 m/yr) into Cenozoic time, or even decreases them, for example by 10 times, then Lake Baikal should have been divided by a sedimentary connecting bridge. However, this did not occur, due to the existence of circulating currents on the floor of Lake Baikal [10]. They truncate the lower part of the alluvial cone, and the washed out sediments are redistributed on the subhorizontal surface of the abyssal trough in the form of a fine layer. The alluvial cone of the Selenga River, in the same way as for other sedimentational bodies of similar type in seas and oceans, is related to the first global level of avalanche sedimentation distinguished by Lisitsyn [7]. Nearly $1 \cdot 10^6 \text{ km}^3$ sediments were accumulated over a short interval of time (a few million years), by approximate calculation. This quantity is commensurate with data for other regions for Cenozoic time, for example, the Rhône: $1 \cdot 3 \cdot 10^5 \text{ km}^3$; the Danube: $1 \cdot 3 \cdot 10^6 \text{ km}^3$, etc. [7].

The region of the Upper Angara delta has a different structure. It is second in importance of supply of material to Lake Baikal. From the shoreline to the abyssal plain, which lies at a depth of 800 m, the underwater extent of the delta extends over 45-50 km. The surface of the shelf floor changes to continental slope here without expressed edges. Sediments carried out from the Upper Angara fill the northern part of the Baikal depression over the entire width (25-30 km), not forming lenticular bodies. The layers of the floor are very complete, and parallel to the surface. They penetrate into the side of central part of the Baikal depression. At the foot of the continental slope is found a bank, hypothetically formed of sandier sediment varieties. Several terraces are noted roughly in the middle part of the continental slope, where the block adjacent to the shore is lowered. It is possible that their formation is caused by sediment compaction.

Underwater channels are sharply expressed here up to the 100-m isobath, and they are absent below it. Transverse to the strike of the depression, the trough floor presents a slightly concave downwards surface. Thus, middle-upper Pleistocene and Holocene deposits in the Northern trough of Lake Baikal do not form an underwater alluvial cone, but a later complex of infilling sedimentational traps with their characteristic structural features [14].

The alluvial cone of the Upper Angara is supposedly noted in the Eo-Pleistocene-lower Pleistocene complex of rocks of this region. The central part of the alluvial cone is designated here, with a central uplift, lowered limbs, primary channel, and alluvial banks. The methods of seismic exploration did not permit good illumination of the internal structure. However even such individual signs make it possible to propose that a deep water alluvial cone of the Upper Angara River existed in Eo-Pleistocene-early Pleistocene time. Subsequently, at the start of the Eo-Pleistocene, a relatively deep water basin was created. This confirms an earlier conclusion on the formation of the North-Baikal trough at boundary of Neogene-Quaternary [11].

Let us compare the data with one of the most studied underwater alluvial cones of the Mississippi River [16, 17, etc.]. It extends approximately 600 km from the modern Mississippi delta to the abyssal trough of the Gulf of Mexico. The cone is represented by individual lenticular bodies (blades) of detrital material. Lenses 150-180 m wide are a few hundreds of meters thick. Younger sediment bodies cover the more ancient. The lens surface is crosscut by a series of underwater channels, and a main channel and a group of fine channels are distinguished. The first of these has depth of a few tens of meters for a width of 3-4 km. Its depth and width decrease towards the sea. The underwater channels are filled

by sediments, whose layers are inclined against the underlying surface. The channels are framed by thin banks.

The underwater alluvial cone of the Mississippi River, as is the Selenga River, is complicated by a whole series of fractures of different amplitudes. Slump bodies are noted on its frontal parts. A very high rate of sediment accumulation is established for late Wisconsin time (10,000-15,000 years), from $11.75 \text{ m}/10^3 \text{ years}$ (in the middle part of the cone) to $6.46 \text{ m}/10^3 \text{ years}$ (on its base) [17]. The upper Wisconsin lens is found out to sea in relation to the more ancient lens.

The underwater alluvial cone of the Danube River has a similar structure [4, 13, etc.]. Lenses of sediments of a few hundreds of meters thick are traced here over an area $\sim 50,000 \text{ km}^2$. The outer edge of the cone reaches the central regions of the deep water Black Sea depression. The dip of the continental slope surface formed by the alluvial cone slopes very mildly and does not exceed $1-2^\circ$. The total thickness of the alluvial cone deposits is 3.0-3.5 km. The primary underwater channel for the carrying out of material, framed by small walls, is observed in the body. Other large underwater alluvial cones of the Orinoco, Rhône, and Ebro rivers have similar internal structure [15, 19, etc.].

Thus, the lens forming structure of the sediment cover is characteristic for a whole series of underwater parts of deltas. The formation of individual lenses causes the migration of the underwater channels feeding in the terrigenous material. The channels themselves are expressed in the form of mildly sloping depressions, formed by parallel banks. After active delivery of material ceases, they are filled by young sediments. Interbedding in the section of complexes of underwater river channels, alluvial banks and other fine sedimentational bodies creates complicated internal structure. This is typical both for deep water cones, and for continental cones [5, 12, etc.]. The alluvial cones have fan-shaped form and build up the shelf and continental slope. Currents of liquified sediment material are characteristic of them [18]. These rework earlier deposited layers. Slump bodies form as a result of such displacement of material, the primary structure of which is not preserved. They are principally correlated to the continental slope. Some support is probably necessary for their arrest. The steep dip angles of horizons inside the lenticular bodies are secondary. They arise as a consequence of post-sedimentational tectonic subsidence induced by pulses of short term subsidence of the basin floor, which captures the edge parts, and in particular the zone of formation of the alluvial cone.

The length of underwater alluvial cones varies. It is a function of basin size and the presence of a system of underwater currents in it. In inland, relatively small basins with circulatory currents (Baikal-Selenga), the alluvial cone forms a short steep continental slope. Large open basins have extended alluvial cones, and the continental slope is mildly sloping (Gulf of Mexico-Mississippi, Black Sea-Danube). It is necessary to note that the continental slope is primarily created by tectonic motions, and the lenticular body of the alluvial cone complicates and accretes to it.

The two main arteries feeding terrigenous material form different types of sedimentational bodies within Lake Baikal. The Selenga River forms an alluvial cone, while the Upper Angara forms a lateral infilling complex. The cause of this difference may include the quantity of introduced material. When it is great, then the sediment acts as a more free-flowing body and is very rapidly unloaded close to the shore line. If the quantity of introduced sediments is not great, then they acquire the properties of a viscous fluid, and they spread over great distances [2]. The Selenga serves as an example of the first case, and the Upper Angara as an example of the second.

The angle of the river's approach to the shore line plays an important role in the formation of one or another type of sedimentational bodies in elongate basins. The Selenga River abuts almost perpendicularly against the shore of Lake Baikal, and its runoff forms a thick bodied alluvial cone. The mouth of the Upper Angara is orientated along the strike of Lake Baikal, the alluvial cone is practically untraced, and all of the material is dispersed into the abyss.

The width of the shelf has a significant value in defining the range of forms of sedimentational bodies. The side of the Baikal depression was formed as a result of tectonic subsidence by fractures. Therefore, the shelf here is narrow. In the central depression, where large fractures are absent, the shelf is a little bit wider. Material is transported very rapidly across the narrow shelf, and it already begins to precipitate within the limits

of the continental slope, forming the lenticular bodies of the alluvial cone. For a wide shelf, the sediments are distributed over its area beforehand, and only then are transported onto the slope by numerous fine underwater channels. Therefore thick bodies of an alluvial cone cannot be formed in such conditions.

It is certain that other processes (the character of tectonic motions of surrounding regions, climate, variations of sea or lake level, etc.) are also superimposed on the development of alluvial cones.

LITERATURE CITED

1. L. A. Vanyakin, M. A. Stor, and V. A. Volkov, "A test of joint utilization of NSP data and deciphering of satellite photographs for the study of Lake Baikal and Pribaikal'ya," in: Materials of the 7th Scientific Conference of Graduate Students and Young Scientists [in Russian], Sekts. Geofiz. (1980), pp. 16-23.
2. N. V. Esin and A. E. Shlezinger, "The flow of viscoplastic sediment, erosion by sediments of the Seas and Oceans (Thesis Reports of the 7th All-Union School of Marine Geology) [in Russian], Vol. 1 (1986), pp. 186-187.
3. S. M. Zamaraev and V. V. Samsonov, "The geological structure and the oil and gas potential of the Selenga depression," in: The Geology and Oil and Gas Potential of Eastern Siberia [in Russian], Gostoptekhizdat, Moscow (1959), 435-474.
4. R. A. Kazantsiev and R. V. Shainurov, "The alluvial cone of suspended flows of the Danube underwater canyon," Geomorfologiya, No. 3, 79-82 (1978).
5. J. Curray and D. Moore, "Sedimentary and tectonic processes in the Bengal deep water alluvial cone and the Bengal geosyncline," in: The Geology of Continental Margins, Vol. 2. [in Russian translation], Mir, Moscow (1978), pp. 327-339.
6. V. V. Lamakin, "Neotectonics of the Baikal depression," in: Tr. GIN, No. 187, (1968).
7. A. P. Lisitsyn, "Avalanche sedimentation in seas and oceans. Report 1," Litol. Polezn. Iskip., No. 6, 3-27 (1983).
8. N. A. Logachev, I. V. Antoshchenko-Olenev, D. B. Bazarov, et al., Mountains of Pribaikal'ya and Zabaikal'ya [in Russian], Nauka, Moscow (1974).
9. L. R. Merklin, V. E. Milanovskii, V. I. Galkin, and M. V. Zakharov, "Structure of the sedimentary sequence and basement relief," in: Geologic-Geophysical and Underwater Investigations of Lake Baikal [in Russian], IO Akad. Nauk SSSR, Moscow (1979), pp. 104-110.
10. I. B. Mizandrontsev, "'Hydrodynamic concentration' N. M. Strakhov and sediment formation in Baikal," Late Cenozoic History of Lakes in the USSR [in Russian], Nauka, Novosibirsk (1982), pp. 11-18.
11. V. G. Nikolaev, L. A. Vanyakin, V. V. Kalinin, and V. E. Milanovskii, "the structure of the sedimentary cover of Lake Baikal," Biol. MOIP, Otd. Geol., 60, No. 2, 48-50 (1985).
12. G. E. Reinek and I. B. Singkh, Features of Terrigenous Sediment Accumulation [in Russian], Nedra, Moscow (1981).
13. Tectonics of Meso-Cenozoic Deposits of the Black Sea Depression [in Russian], Nedra, Moscow (1985).
14. A. E. Shlezinger, "Rock complexes of sedimentational basins according to materials of seismostratigraphic analysis," Geol. Geofiz. No. 1, 12-18 (1987).
15. H. Belderson, N. H. Kenyon, A. H. Strike, and C. D. Pelton, "A braided distributary system on the Orinoco deep-sea fan," Marine Geol., 56, No. 1-4, 195-206 (1984).
16. A. H. Bouma, C. E. Stelling, and J. M. Coleman, "The Mississippi fan: internal structure and depositional processes," Geo-mar. Lett. 3, No. 3-4, 147-153 (1983-84).
17. "Challenger drills the Mississippi fan," Geotimes, No. 7, 15-18 (1984).
18. D. G. Howell and W. R. Normark, "Sedimentology of submarine fans," in: Sandstone Depositional Environments, Tulsa, OK (1982), pp. 365-404.
19. C. H. Nelson, A. Maldonado, F. Coumes, et al., "The Ebro deep-sea fan system," Geo-mar. Lett., 3, No. 2-4, 125-131 (1983-84).

SOME RULES FOR THE DISTRIBUTION OF BOTTOM SAND MICROFORMS IN THE MARINE SHORE ZONE

R. D. Kos'yan

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On the basis of results of natural observations in the shore zone of the sea, some rules for the distribution of bottom microforms and the composition of the sediments composing them are recognized. They are dependent on the characteristics of the surface roughness and the effect of massive cylindrical footings. Described first are the occurrences under natural conditions of rolling grain ripples, and the configuration and size of bottom forms from the wave disintegration zone.

Wave ripples are the most widespread microforms on the bottom of the shore zone of the sea. These forms may occur over significant parts of the continental shelf, from the shore line to relatively great depths.

The ripple geometry and the connection of their sizes with the motion of water masses present interest for understanding alluvial transport, for estimating the attenuation of waves as a result of friction on the bottom, and for interpreting ancient conditions of wave formation.

In this article, bottom sand microforms occurring in the shore zone of the sea are described on the basis of material from natural observations, and some general rules for the distribution of bottom forms and the composition of the sediments composing them are recognized. They are dependent on the character of the surface roughness and the presence of massive footings.

Natural observations were carried out during international experiments by the SEV member-nations, "Kamchiya-78," "Shkorpilovtsy-82," and "Shkorpilovtsy-83." In these experiments, the efforts were conducted on a single sand interval from the Bulgarian coast of the Black Sea in the different years. The bottom relief in the polygon region is rather uniform, with isobaths almost parallel to the shore line. The average slope of the bottom at depths from 0 to 18 m reaches approximately 0.017. More than 95% of the bottom sediment particles occur in the coarse and medium grained sand fractions in the upper part of the underwater profile, at depths less than 2.5 m. With increased depth their percent content decreases, and already at depths of 8 and 10 m more than 90% of particles occur in the fine grained fraction. For $H \geq 12.5$ m, the average sediment size is increased due to growth in the percent content of broken shells, and at depths of 15-18 m, as well as near shore, more than 90% of the bot-

TABLE 1. Range of Variation in the Characteristics of Orbital Velocity, Coarseness of Bottom Sediments, and Bottom Form Parameters at Time of Natural Observations

Experiment No.	Characteristics of ripple activity	H, m	D, mm	λ , cm	h , cm	U_m , m/sec	T, sec
"Kamchiya-78"	Active	0.7-4.3	0.203-0.433	15-300	3.5-40.0	21-79	3.6-6.3
"Kamchiya-78"	Passive	0.7-4.3	0.201-0.642	18-32	3.0-5.5	—	—
"Shkorpilovtsy-82"	Active	2.2-3.1	0.273-0.540	17-45	2.5-9.0	25-45	4.5-4.6
"Shkorpilovtsy-83"	Active	2.6-4.5	0.203-0.296	20-250	4.0-50.0	16-64	2.7-4.3
"Shkorpilovtsy-83"	Passive	4.5-18.0	0.171-0.877	16-120	1.0-14.0	—	—

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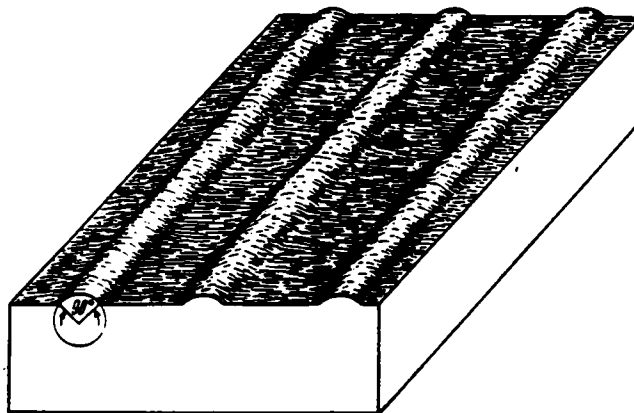


Fig. 1. Internal view of bottom forms corresponding to the description of rolling grain ripples.

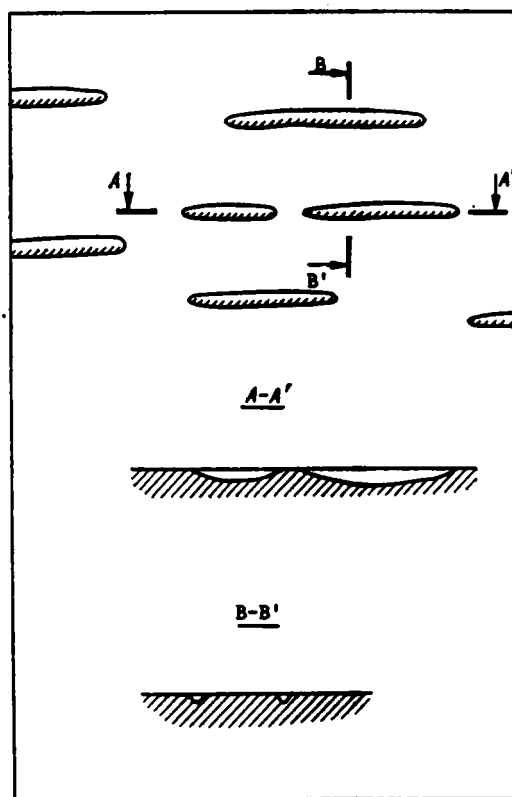


Fig. 2. Bottom forms under disintegrating waves.

tom particles are greater than 0.3 mm. The average specific weight of the sediment is $\sim 2.65 \text{ g/cm}^3$.

At the time of approach to shore, the surface waves were smoothly transformed, experiencing single-stage disintegration for weak and moderate roughness and two-stage disintegration for strong roughness. The boundary of active* and passive ripples was displaced with depth dependent on the power of the roughness, and in proportion to its weakening the greater part of the bottom of the shore zone appeared to be covered by passive forms.

A map of the experimental polygon and the distribution of its observation points in the different years is given in [3].

*We will term as active ripples those which correspond to the wave environment at the moment of their inspection. Ripples which formed by roughness preceding the observation period we will term passive.

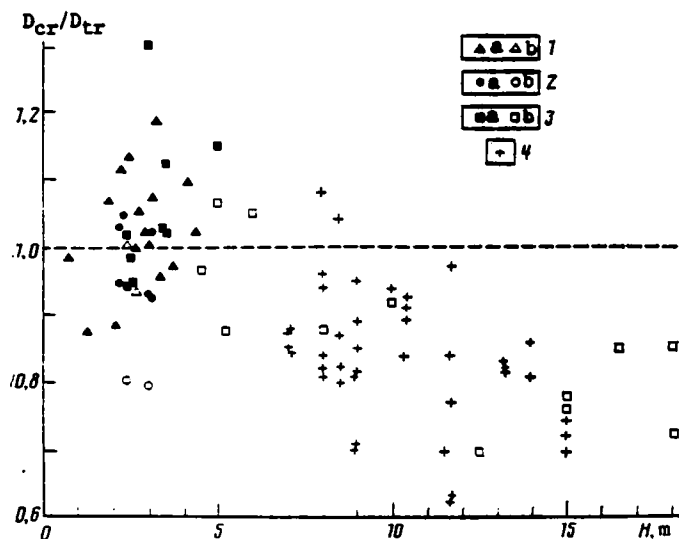


Fig. 3. Values of D_{cr}/D_{tr} at various depths, from experimental data: 1) "Kamchiya-78"; 2) "Shkorpilovtsy-82"; 3) "Shkorpilovtsy-83"; 4) results of measurements on part of the North African shelf. a) denotes active ripples; b) passive.

TABLE 2. Characteristics of the Granulometric Composition of Sediments Selected at Single Points of the Bottom Surface at Different Times from the experiment "Shkorpilovtsy-83"

Measurement date	H, m	D, mm	γ	α	τ
29.X	2,6	0.27	24.2	-0.67	0.82
6.XI		0.21	24.6	-0.95	1.59
10.XI		0.25	21.1	-0.16	0.51
29.X	3,0	0.27	28.6	-0.34	0.04
4.XI		0.24	20.0	-0.43	0.95
6.XI		0.30	28.0	-0.20	0.51
10.XI		0.29	26.3	-0.07	0.31
29.X	4,5	0.24	27.8	-0.37	0.41
2.XI		0.25	29.4	-0.50	0.41
10.XI		0.23	30.0	-0.73	1.33
2.XI	15,0	0.77	334.9	-0.35	0.61
10.XI		0.82	513.6	-0.05	0.21

In 1978 and 1982 investigations were conducted to depths up to 4 m, in the zone of greatest variability of bottom microforms. In 1983 the observations encompassed the portion of the bottom up to the 18 m isobath.

At a specific time a scuba diver descended under the water and traveled along a cable which was fixed to the bottom and marked by special labels over a determined distance. At designated points he noted the fact of the presence or absence of bottom forms, determined their parameters as an average from tens of those measured, described their form and orientation, and sampled specimens of the bottom sediments. The principal part of the underwater observations described in the present article was performed by the author. A. P. Filippov performed the undersea measurements in 1982.

The criterion which defined ripples as active was their ability to restore their form. For an estimate of this ability, the bottom surface was leveled at the measurement point over an area of $1 m^2$. If after 10 min the parameters of the reforming ripples became as they were before the leveling, then the ripples were considered active. We note that in the first place through a time corresponding to the transit of several surface waves, the length of the sand forms characteristic of the environment was restored. The process of restoration of ripple height lasted longer.

TABLE 3. Characteristics of Sediments Composition Selected from the Different Elements of Bottom Forms (from data of the "Shkorpilovtsy-83" experiment)

Meas. date	H, m	Portion of the ripples, from which the sample was selected	D, mm	γ	α	τ
10.XI	3,5	Crest	0,23	28,4	-0,75	0,99
		Upper portion of the slope	0,23	27,3	-0,67	1,15
		Trough	0,20	24,3	-0,58	1,57
2.XI	5,0	Crest	0,25	26,1	-0,47	0,62
		Upper portion of the slope	0,24	25,8	-0,44	0,65
		Lower portion of the slope	0,23	25,0	-0,47	0,78
		Trough	0,23	24,9	-0,57	0,83
10.XI	16,0	Crest	0,82	204,8	0,28	0,34
		Upper portion of the slope	0,83	206,2	0,13	0,56
		Lower portion of the slope	0,90	392,5	-0,11	0,84
		Trough	0,96	461,6	-0,52	-0,87
2.XI	18,0	Crest	0,73	125,2	-0,38	0,74
		Upper portion of the slope	0,72	106,8	-0,25	1,75
		Lower portion of slope	0,81	202,1	-0,81	1,49
		Trough	1,00	1146,2	-0,42	-0,33

TABLE 4. Characteristics of Sediment Composition Selected at Various Distances from a Footing (from the bottom experiment "Shkorpilovtsy-83")

Meas. date	H, m	Distance from support, m	D, mm	γ	α	τ
4.XI	3,5	0	0,66	169,1	-0,22	-0,70
		10	0,31	35,5	-0,52	0,22
6.XI	2,6	0	0,49	80,2	-0,42	-0,19
		10	0,21	24,6	-0,95	2,59
18.XI	3,1	0	0,31	28,1	-0,29	0,61
		0,5	0,21	20,7	-0,70	2,22
		3	0,28	20,3	-0,47	1,16
		6	0,28	23,7	-0,28	0,85
		9	0,27	22,8	-0,55	0,41

Dried samples of solid particles underwent granulometric analysis. An 18-fractional sieve kit was utilized for this. This covered the size ranges of meshes from 0.063 to 2.5 mm with indexes of geometric progression 1.25-1.27. The characteristics of the distribution of sediment composition were calculated as results of the analysis. In Table 1 are shown the range of variation of the measured ripple parameters and calculations of the characteristics of the composition. More complete data are given in [3].

Ripples with rounded crests and almost flat troughs formed first on the flat bottom. They were first described by Bagnold [6], and named rolling grain ripples. This term is explained by the fact that in the ripple formation the sand grains are rolled over back and forward on the bottom before they are grouped into mobile crests, from which they then fall avalanchelike into depressions of the underlying immobile bottom. Rolling grain ripples were developed and investigated only in laboratory experiments [7, 8, 10, 13]. It was learned that such bottom formations are very unstable, that they are distinguished by small steepness (ratio of the ripple height h_r to its length λ_r reaches < 0.1), and they exist for solid sand particles only within a range of values of liquid shearing velocities U_c from U_c to $2U_c$. Such ripples have not been detected before under natural conditions.

Rolling grain ripples were successfully encountered at sea in 1983, at depths greater than 12.5 m, although only in the passive state, to be sure. Their internal form presented itself as successively equidistant sand bands with rounded flattened crests (in profile, the contour of the crest appeared in the form of an arc of a circle with magnitude $\approx 90^\circ$) and almost flat troughs (Fig. 1). In the form of their profile and their small (from 0.05 to 0.11) steepness they correspond to Bagnold's description [6]. The formation of these unstable ripples may be explained by features of the water area on which they are arranged. Relatively coarse bottom material (average grain size $D = 0.7-0.9$ mm) at these depths was brought into motion only by the very largest surface waves, at the time that the greater part of the orbital velocities had a value less than U_c . In favor of this, the maximum orbital near-bottom velocity (U_m) did not fall outside the limits of the range of velocities for which rolling grain ripples may exist ($U_c \leq U_m \leq 2U_c$).

Then ripples with circular crests are transformed into vortical ripples, which are characterized by steep spiral profiles: by wide troughs, approximating in form the arc of a circle of great radius, and narrow, strongly twisted crests [5, 6, 7, 12, 13]. For each change in the direction of orbital motion, the vortex forming from the lee side of the crest, together with sediments entrained in it, rises upwards into the current sequence. The sand removed from the trough is either settled on a neighboring crest, or it crosses into the suspended state. In the overwhelming majority of cases we encountered vortical ripples. In them, the crests of the passive ripples had as a rule a circular form, and the active a more acute form.

As was noted in [9], the outlines and dimensions of vortical ripple fronts, which are weakly dependent on asymmetry of wave velocities and variations in the directions of wave approach, are determined by the intensity of wave action on bottom. Our observations confirm this conclusion.

Bottom formations of symmetric two-dimensional sand waves with fronts parallel to one another occur during a gale at a significant distance from shore and comparatively great depths for relatively small near-bottom velocities. In proportion to closeness to shore, the depth of sea decreases and the values of near-bottom wave velocities increase. With this, the fronts of the bottom forms become sinuous, with ever increasing phase shift. Close to the zone of form disintegration they have a three dimensional cellular structure without an expressed single front. With further increase of orbital velocities, the bottom is flattened out. However, quite peculiar bottom forms are apparent at the bottom, in the same zone of disintegration. They are distinguished by outlines and sizes from microforms of other portions of underwater profile. The formation of similar forms has not been noted before in the literature.

The approximate internal form of bottom forms from the disintegration zone is shown in Fig. 2. Long flattened crests up to 2 m in length alternate with short (no more than 1 m) steep (no deeper than 0.4 m) troughs - trenches. The correlation of crest and trough lengths varies from 2:1 to 5:1. Their appearance is apparently connected with the existence of hydraulic impacts on the bottom owing to reversing of surface wave crests and corresponding excavation of bottom material. During each half period of a wave, loads were driven in the direction of its propagation to a level layer of the sequence, up to several centimeters. Traction of sand on the floor is alternated with vortical lacing from spinning particles, parallel to one another and perpendicular to the wave front. Flat motion of particles along the crest is interrupted by the approach to the pit-trough, after which the cluster or cone-shaped vortex is ejected into the water sequence.

The usual bottom forms are again apparent closer to shore from the disintegration zone. They have initially a chaotic cellular configuration, and then are increasingly more ordered. Long fronts of forms parallel to one another reform at a sufficient distance from the disintegrating waves. However, between the disintegration zone and shore line the ripples become notably asymmetric and their orientation varies thus, such that the angle between the shore line and normal to the sand wave fronts appears more acute than the corresponding angle between the shoreline and normal to the front of the surface marine waves.

Asymmetric bottom forms and divergence of the general direction of their propagation from direction of wave motion indicates correlation of longshore currents to the place of their detection, and the degree of asymmetry and divergence indicates the power of these currents. With the aid of more detailed observations it is possible to reconstruct a map of the direction of fronts and the asymmetry of the ripples. Rudovskii [11] performed similar work for part of the Polish coast of the Baltic Sea. He was successful in locating a region where discontinuous currents existed in his observations on ripples of a coastal water area.

The distribution of different bottom forms and the configuration of their fronts along the profile of a single similar slope may vary dependent on the power of the gale and the arrangement of the parts of wave disintegration.

After the end of the gale, the sand ripple preserves the traces of wave action on the bottom at some moment in the stage of its attenuation. Therefore it is impossible to judge the microrelief of the bottom for the development of roughness from a map of bottom forms based on calm weather observation.

We also note features of the orientation of bottom forms adjacent to massive vertical stationary footings (diameter 1 m). The presence of such footings changes the direction of

of water flow at the bottom and significantly increases its turbulence [1]. In the zone of significant intensity of wave action on the bottom, its surface at the footing (at a distance roughly equal to the diameter of the footing) appeared flattened out, at the time that bottom forms developed distant from them. For small roughness, the steepness of forms lying close to the footing exceeded the steepness of the distant forms, while their fronts radiated in a fan-shape on all sides.

Comparing sediment composition, samples of which were selected at a single point of the bottom surface at different times, it is possible to note that its characteristics over a period of observations varied significantly. Variation in the average size of bottom sediment particles reached 10% after some time. The remnant statistical moment of the distribution of granulometric composition varied still more strongly. Examples of the change in the composition characteristics from data of the experiment "Shkorpilovtsy-83" are shown in Table 2.

These data indicate that ground maps of the shore zone of the sea based on results of analyses of bottom sediments tests selected one time bear an approximate character. For investigation of sediment flows on different portions of the underwater slope, as well as for the study of dynamics of ripples, characteristic of the bottom material, it is necessary to determine characteristics simultaneously with other measurements. Neglect of the variability of sediment composition over time may lead to incorrect interpretation of observation results.

Mechanical differentiation of the composition of material along the length of the sand form occurs in the process of ripple formation at the shore zone of sea. The ratio of average size of sediment grains of the crest and trough (D_{cr}/D_{tr}) for passive ripples (Fig. 3) decreases with depth. For greater clearness, results of measurements of values D_{cr}/D_{tr} for passive ripples are shown in Fig. 3. They were obtained from investigations on part of the North African shelf [2]. The inverse picture is observed for active ripples (Fig. 3). For rather strong wave action on bottom, the average size of sand particles on crest as a rule is larger than in the trough. The value of D_{cr}/D_{tr} reaches particularly large (up to 1.3) values close to the zone of surface wave disintegration.

Tests of surface ground taken from various points of the ripple slope (Table 3) indicate that the characteristics of distribution of sediment composition primarily vary smoothly along the slope from crest to trough.

The obtained results may be explained by the following example.

At the onset of ripple formation, for relatively small near-bottom velocities, only fine particles of the polyfractional bottom material proceed into motion. The moving sediments move away from the trough and are accumulated on the ripple crest. The coarser particles remain in the trough, and at this stage their average size is greater than the size of the crest sediments.

With strengthening of the gale an increasingly greater part of the bottom material proceeds into motion, and sediments of all represented sizes will be involved in it. The vortex forming in the trough of the bottom form together with the sand particles entrained by it rises from the bottom from the trough is accreted to the neighboring crest, while fine sediments transfer to the suspended state. In this situation the sediments on the crest appear coarser than in the trough.

At the end of the gale, the coarser particles roll down from the crest to the trough under the influence of gravity, increasing the average size of sedimentary material. Therefore, in passive ripples the value D_{cr}/D_{tr} is most often less than one. Thus, the sign of the deviation of the value D_{cr}/D_{tr} from one is determined by the intensity of wave action on the bottom.

At depths less than 5 m, in regions of significant transformation and dissipation of wave energy, the bottom sediments are generally well sorted (the average coefficient of variation of composition for 126 tests γ is equal to $31.8 \pm 1.0\%$). The sorting of the material of the crest, slope, and trough in these regions often has a similar value (Table 3). The overall sorting of the material worsens with increased depth. There, where broken shells appear in the bottom sediments, the value of the coefficient of variation in the composition exceeds 100%. The sorting of material in the troughs of bottom forms appears particularly low here. The coefficient of the variation in the sediment composition in the trough may

reach values above 100% and significantly exceed the variation on the crest (Table 3). On such grounds the values of D_{cr}/D_{tr} have the smallest value for the wide range of bottom particle sizes.

The coefficients of asymmetry α and excess of τ of distribution of particle sizes on the test portion were basically small. As result of analysis of 145 tests, $\alpha = -0.342 \pm 0.032$; $\tau = 0.466 \pm 0.083$. This implies that the granulometric composition of bottom sediments conforms to lognormal distribution [4].

The average size of the bottom particles is significantly (by 2 or more times) increased alongside the massive footings during a gale. Comparison of material taken at different distances from the footing from bottom ground tests (Table 4), make it possible to note the following: at a single isobath at a single time, the coarsest material is accumulated at the footing. At a distance of 0.5 m from the support, the average size of the sediment particles has the smallest value. For a distance of 3 m and more, the composition of sediments is stabilized.

In the presence of the footing, which adds turbulence to the water sequence, the quantity of particles transferring from the bottom to the suspended state is increased [1]. Principally the lighter sands are suspended, therefore the coarse particles are accreted alongside the footing. Turbulization of the near-bottom region is decreased with distance, and the suspended loads settle to the bottom. Therefore, apparently, here is a relatively small average size of sand grains. At a distance greater than 3 m, the additional turbulent agitation of the water mass becomes insignificant, and the presence of the footing is not reflected in composition of bottom material.

We formulate the following basic conclusions.

Distribution of different bottom forms and the configuration of their fronts along the profile of a single underwater slope may vary dependent on the gale's power and the position of portions of wave disintegration.

In proportion to the strengthening of wave activity, bottom forms with fronts parallel to one another form first, and then their fronts become increasingly sinuous. The forms subsequently transform to a cellular three-dimensional configuration, and finally the bottom is flattened. In the zone of wave disintegration, new forms arise on the bottom which are distinguished from those described earlier. For the first time descriptions of the configuration and sizes of bottom forms of the wave disintegration zone are cited.

At relatively large (>12.5 m) depths on a sand bottom, bottom forms occur which by their configuration correspond to rolling grain ripples. Similar bottom formations have not been detected before in natural conditions.

Close to massive footings, the sizes and orientations of bottom forms, as well as the composition of bottom sediments, are significantly altered.

Deviation of the direction of bottom form fronts from surface waves fronts and asymmetry of microforms are most significant in zones where near-shore wave currents are active.

The composition of bottom sediments may vary strongly at a single point of the underwater shore slope.

The value of the ratio of material grain size on the crest and trough of passive ripples is a rule less than one. For active ripples it is greater than one. The values of this ratio depend on the intensity of wave action on the bottom and the sediment sorting.

LITERATURE CITED

1. S. M. Antsyferov, T. Basin'ski, R. D. Kos'yan, et al., Shore Processes of a Nontidal Sea [Russian translation], No. 5, Prace IBW PAN, Gdansk (1978), pp. 211-228.
2. R. D. Kos'yan, Results of Lithodynamic Investigations in the Near Shore Zone of Part of the North African Shelf [in Russian], Dep. VINITI, No. 5402, Moscow (1983).
3. R. D. Kos'yan, Results of Natural Investigations of Ripples on Sandy Coasts [in Russian], Dep. VINITI, No. 2319, Moscow (1985).
4. G. G. Rozhkov, Z. N. Ipatov, O. V. Kolobzarov, and R. N. Staison, "Fractional sieve granulometric analysis," *Litol. Polezn. Iskop.*, No. 6, 121 (1973).

5. J. R. L. Allen, Geol. Soc. London, 136, 673-682 (1979).
6. R. A. Bagnold, Proc. R. Soc. London, 187, 1-16 (1946).
7. M. R. Carstens, F. M. Neilsen, and H. D. Altinbilek, "Bed form generated in the laboratory under an oscillatory flow: analytical and experimental study," U.S. Army Corps. CERC, Tech. Memo No. 28 (1969).
8. M. Manohar, "Mechanics of bottom sediment movement due to wave action," U.S. Army Corps Eng. Beach Erosion Board, Tech. Memo No. 75 (1955).
9. E. Matsumoto and I. Takeda, Ann. Rep. No. 5, Inst. Geosci. Univ. Tsukuba, 39-42 (1979).
10. M. C. Miller and P. D. Komar, J. Sediment. Petrol., 50, 173-182 (1980).
11. S. Rudowski, "Zmarszczki w strefie przybrzeża południowego Bałtyku," Acta Geol. Polon, 12, No. 4 (1970).
12. J. F. A. Sleath, "A contribution to the study of vortex ripples," J. Hydraul. Res., 1, No. 3, 315-328 (1975).
13. J. F. A. Sleath, "On rolling grain ripples," J. Hydraul. Res., 14, No. 1, 69-81 (1976).

ROLE OF EOLIAN TERRIGENOUS MATERIAL IN SEDIMENT FORMATION

V. S. Savenko

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In the article, we discuss the role of eolian terrigenous material in oceanic sediment accumulation. We review the existing information on the concentration of terrigenous aerosol in the atmosphere over the oceans and on the intensity of dry and humid deposition.

The processes of mobilization, transport, and deposition of airborne dust has recently been the subject of study by members of the geological-geographical disciplines, since many important phenomena occurring in the atmosphere, hydrosphere, and lithosphere are associated with these processes [4, 5, 17, 24, 33, 39]. One aspect of the study of the eolian migration of material concerns explaining the role of migration in sediment formation. The principal sources of atmospheric aerosol (the arid and semiarid regions of the continents) are characterized by low water flow; aqueous migration of material in such areas takes a back seat to processes of eolian mobilization and transport of sedimentary material. There are fairly persuasive arguments indicating the importance of atmospheric aerosol in sediment formation. With regard to the pelagic regions of the ocean in particular, many authors are inclined to believe that this delivery route for sedimentary material is either predominant or is of same importance as fluvial discharge [6, 7, 13, 23, 24]. Within the last two decades, new, fairly extensive data has accumulated on the dust load of the air over the continents and oceans. Information has been obtained on the granulometric composition of aerosols and we have refined the rate parameters for the weathering of aerosols from the atmosphere as a result of dry settling and wash-out of the air by precipitation. Much has been accomplished in the study of the processes of generation and transport of airborne dust. All of this allows us to refine existing estimates of the supply of eolian suspensions to the seas and oceans and allows us to refine our conception of the relationship between this and other sources of sedimentary material.

The Formation of the Terrigenous Aerosol and its Distribution in the Atmosphere

The steppes and the deserts are the fundamental regions for the generation of terrigenous aerosols. K. Ya. Kondrat'ev and V. D. Pozdnyakov [19] distinguished between global and local (regional) sources depending upon the magnitude of the processes involved in the generation of terrigenous aerosols. They assign the Sahara region in the north of Africa and the Gobi and Takla Makan deserts in Asia to the first group of sources and assign to the second group

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the desert and steppe regions of Central Asia, northwestern Kazakhstan, and northern Cis-Caucasia, the arid regions of western Europe, regions where loess-type loams occur in northern Iran, the deserts of the Arabian Peninsula, Pakistan, and northwestern India, the arid and semi-arid regions of Mongolia and China, the deserts of Kalahari in the south of Africa and Ogaden and Hubi in the northeast of this continent, the northwestern and central desert regions of Australia, and also the arid regions of Mexico and the south of the USA. These extensive areas are characterized by high dust content in air, which, by circulating within the given territories, brings about a large-scale redistribution of terrigenous material.

The actual scales of eolian migration of matter have been discovered fairly recently thanks to information on the formation and transport of large-scale dust clouds obtained with the aid of artificial earth satellites. As a result of these observations, it was established that the area of an isolated dust cloud is from tens of thousands to several millions of square kilometers for a mass of a hundred thousand to several million tons [11, 18]. The numerical data characterizes, so to speak, the instantaneous mass of the dust cloud, and the resulting magnitude of eolian transport turns out to be somewhat higher. For example, dust storms in 1928, 1960, and 1969 to the south of the ETS transported 9-15 million tons of matter over the course of several days, the dust cloud observed over the Aral Sea on May 22, 1976 transported approximately 15 million tons of dust, while the dust cloud which formed in the region of the Gobi and Takla-Makan deserts transported approximately 0.5 million tons of dust over the course of five days in April of 1976 [18, 19]. The processes of generation of terrigenous aerosol are strongest in the Sahara region, where 60-200 million tons of matter enters into the air yearly [21]. The rate of movement of dust clouds is on the order of 1000-2000 km/day [13, 19]; this makes possible the transport of fairly coarse material to a distance of a thousand kilometers. The existence of strong out-going air currents which rise to altitudes of 1.5-5 km in the regions of aerosol generation facilitates such transport; further transport of aerosols can take place at these altitudes. As a result of gravitational settling, mineral dust outbreaks from the arid regions undergoes granulometric sorting: particles with dimensions of 100-500 μm are deposited within the first 500-1000 km from the region of generation. The dimensions of the terrigenous aerosol in more remote regions do not, as a rule, exceed 10-20 μm [6, 50].

Before proceeding to a discussion of the quantity of terrigenous aerosol in the atmosphere over the ocean, it is necessary to briefly give attention to the methodology involved in measuring the concentration of mineral dust in the air, since information obtained by different methods is not always comparable. It is common to infer the weight concentration of atmospheric aerosol on the basis of direct measurements (collection in meshes, filters, or impactors) or by using indirect indicators of the dust load of the atmosphere based primarily on the amount of light attenuation. The various means of measuring the number of particles in a unit volume of air should be classified as indirect methods, since they do not allow one to carry out a determination of the densities of the particles. The calculation of mass concentration of airborne dust can be of an extremely approximate character because of this.

Among the direct methods, the use of impactors and filters which effectively retain particles with dimensions of more than 0.1-0.2 μm (particles which constitute a significant fraction of the total mass of aerosols) gives the most reliable results. When using mesh (the majority of the data for the seas and oceans were obtained in this manner), interception of the particles takes place when the particles collide with the threads of the meshes and the capture efficiency depends strongly upon the dimensions involved: the efficiency of capture of aerosols with dimensions of approximately 1 μm is all of 15% of the efficiency of capture of particles larger than 6 μm [49]. In view of the fairly significant space-time variability associated with the granulometric characteristics of the aerosols, the assumption [51] of an overall 50% capture efficiency for particles larger than 1 μm should be considered only a very rough approximation. Aside from this, the very methodology for mesh collection of aerosols presupposes treatment of the meshes with distilled water, as a result of which the sea salts are dissolved and the insoluble residue consists primarily of terrigenous material. As a rule, differentiation into marine (soluble) and terrigenous insoluble aerosols does not take place during filtration when using an impactor collector. This should be kept in mind when comparing results obtained by different methods.

Reliable data on the average concentration of mineral dust exists at present for the territories of the USA and the USSR, but the large areas of these two countries allow us to make assumptions concerning the level of global dust load for the continental atmosphere within various climatic zones. The average yearly concentrations of aerosols at rural ob-

TABLE 1. Content of Mineral Dust in the Air over Seas and Oceans

Region of aerosol collection	No. of samples	Conc., $\mu\text{m}/\text{m}^3$		Published source
		Average	Content limits	
ATLANTIC OCEAN				
Northern Atlantic (55-40°N)	11	0,004	0,001—0,01	[52]
Northern Atlantic (30-10°N)	11	0,52	0,13—0,96	[15]
Equatorial and Southern Atlantic (10°N-20°S)	19	0,66	0,33—1,80	[40, 42]
Near Western coast of Europe	17	0,11	0,003—0,69	[43, 44, 52]
Near Coast of Northwestern Africa	25	7,0	0,17—26	[40, 42—44]
Barbados Island	180	2,5	0,2—10,2	[53]
Mediterranean Sea	13	0,24	0,03—1,15	[61]
INDIAN OCEAN				
Water area of the Zondsk Archipelago	11	0,26	—	[14]
Southern margin of the Arabian Sea	38	0,34	—	[14]
Southwestern and northeastern regions of the Indian Ocean (10°N-30°S)	15	0,71	0,01—4,4	[40]
Near coast of Southern Africa	2	2,4	0,45—4,3	[40]
Bay of Bengal	39	2,24	—	[40, 47]
Near western coast of Australia	15	0,18	—	[14]
PACIFIC OCEAN				
Central and eastern regions of the northern portion of the Pacific Ocean (40-30°N)	8	0,46	0,04—0,95	[46]
Southern regions of the Northern portion of the Pacific Ocean (30-15°N)	20	0,68	0,19—0,88	[15]
Equatorial regions of the Pacific Ocean (15°S-15°S)	59	0,25	0,03—1,2	[15, 57]
Northern regions of the Southern portion of the Pacific Ocean (15-40°S)	17	0,29	0,06—0,8	[15]
South-China Sea	3	0,21	0,15—0,31	[40]
Sea of Japan	1	0,02	—	[40]
A Selection of samples from filters				
ATLANTIC OCEAN				
Northern Atlantic (Station C, 55°45' S, 35°30' W)	—	1,3	—	[16]
Central and Northern Atlantic (64-28-22°N)	109	1,30	—	[56]
Tropical and equatorial Northern Atlantic (28-22°-0° N)	22	36,6	—	[56]
Tropical Atlantic (30-5° N)	25	15,8	0,35—107,0	[41]
Equatorial and Southern Atlantic (5° S-20° S)	10	0,34	0,11—0,61	[41]
Tropical Northern Atlantic: Sal Island	71	29,8	—	[59]
Barbados Island	78	20,5	—	[59]
Miami	74	8,08	—	[59]
Tropical and Central Southern Atlantic (5-35° S)	35	1,35	—	[56]
Same, and Cape of Good Hope	40	1,22	—	[56]
Mediterranean Sea	13	4,57	—	[56]
INDIAN OCEAN				
Indian Ocean (7°N-45° S)	5	7,20	—	[56]
Bay of Bengal				
PACIFIC OCEAN				
Pacific Ocean (28° N-40°S)	24	0,58	—	[56]
Straits of Malacca, South-China Sea, and Phillipine Sea	6	1,51	—	[56]

servation stations in the USA amount to 20-80 $\mu\text{g}/\text{m}^3$ with the most common values at 30-40 $\mu\text{g}/\text{m}^3$ [22]. According to the data presented in a report [25], a broad zonality is clearly outlined; this zonality is characterized by an increase in the concentration of dust in the air from 20-100 $\mu\text{g}/\text{m}^3$ in the steppe zone to 100-150 $\mu\text{g}/\text{m}^3$ in the arid steppes and desert regions of Kazakhstan and Central Asia. In regions where humid soils are common or where snow cover exists, an increase in the wind velocity exerts a slight effect upon the dust load of the atmosphere, since, for dry soils, the dust load of the air increases sharply for wind velocities over 4 m/sec (at an altitude of 1 m): at a wind velocity of 5 m/sec, dust load exceeds the background level corresponding to velocities of 0-4 m/sec by a factor of three [25].

TABLE 2. Deposition of Eolian Terrigenous Material

Type of deposition	Thickness (g/m ²) of material	Published source
Saharan dust in Europe March 9-12, 1901 (over an area of 470 thousand km ²)	3,8	[34]
Reddish-yellowing snow on the vicinity of Mt. Kaluga in April, 1907	0,4	[28]
Mineral dust on the northern coast of the Caspian Sea over the course of three summer months	1,4	[3]
Eolian dust on the eastern coast of the Middle Caspian (yearly average)	~19	[7]
Eolian dust on the northern coast of the Kola Peninsula (yearly average)	0,11	[2]
Insoluble eolian dust in January, 1981 in the region of Oceanographic Station C (55°45' S, 35°30' W)	0,14	[32]
Insoluble eolian dust in January, 1981 in the region of Oceanographic Station C (55°45' S, 35°30' W)	0,08	[16]
Mineral dust on glaciers of Antarctica, Greenland and alpine temperate latitudes (average intensity)	5,5·10 ⁻⁴ —5,5·10 ⁻³	[63]
Mineral dust in the region of the Kret Station (in Greenland) (intensity averaged for 200 years)	~6·10 ⁻⁵	[48]
Insoluble aerosol on the ice cover of Antarctica (average intensity of sediment)	0,6—6·10 ⁻⁶	[20, 26]

Direct measurements of the dust load of the atmosphere over the ocean have come into use comparatively recently, and the bulk of information gathered is concerned with range-of-visibility determinations. These determinations were conducted at institutes for various purposes over the course of many decades. Thanks to these observations, there are now maps of the frequencies of recurrence of dust clouds [1] which can serve as a quantitative characterization of the relative dust load of different regions of the World Ocean.* In Table 1, we present a compilation of existing data on direct measurements of concentrations of terrigenous (undissolved) aerosol in the atmosphere over the ocean. What immediately catches the eye in this table is the fairly uniform values for the average concentrations of mineral dust over extensive water areas located outside the zone of direct influence of the most active continental sources of terrigenous aerosol: according to filtration data, the typical concentration of mineral dust in such regions is 1.2-1.5 $\mu\text{g}/\text{m}^3$. According to mesh collections, the typical concentration is somewhat less (0.1-0.7 $\mu\text{g}/\text{m}^3$); this result was due to the lower efficiency (~50%) [45] of the latter method. A value of $1.5 \pm 0.5 \mu\text{g}/\text{m}^3$ can thus be assumed to be a typical average concentration of mineral dust in the atmosphere over the ocean outside the zone of influence of the most intense continental sources of terrigenous aerosol.

It is significantly more difficult to estimate the average concentration of mineral dust in the air over a water area existing in close proximity to a major source of generation of eolian material, since there are strong space-time variabilities at such localities. Judging from filtration measurements (see Table 1), the usual level of dust load is in the range of 10-40 $\mu\text{g}/\text{m}^3$ for the atmosphere of the Tropical and Equatorial Atlantic; this atmosphere exists under conditions of constant influence from Sahara, a large-scale source of eolian material. A concentration of $25 \pm 15 \mu\text{g}/\text{m}^3$ can probably be assumed as an average for the region. It should be noted that, according to the data from mesh collection, the influence of the Sahara is strongly perceived only near the coast, whereas the filtration samples indicate a high degree of dust load over significantly larger areas. This is connected with the fact that the coarse fractions of the aerosols which are retained by meshes and filters with identical efficiencies, settle near the coasts, while the finer fractions which show low capture coefficients when mesh collection is used, pass down into the depths of the ocean. Other regions of the ocean located near less intense sources of terrigenous aerosol show a lower average level of dust load consisting of approximately $5 \pm 3 \mu\text{g}/\text{m}^3$ (see Table 1).

Deposition of Terrigenous Eolian Material

The most reliable data on the intensity of deposition of eolian material was obtained

*L. G. Bondarev [6] attempted to use data on the frequencies of recurrence of dust clouds to evaluate the scales of delivery of mineral dust to the oceans, but they have admitted an error in translating the dimensions of $\mu\text{g}/\text{m}^3$ as mg/m^3 (i.e., a thousandfold greater). Moreover, an assumption of values of 5-10 μm for the average dimensions of aerosol particles was not corrected.

on the basis of direct methods: collection of dry deposits during aerial surveys, separation of suspended matter accumulated from rain and snow precipitation, and determination of the quantity of suspended matter accumulated on glaciers over a specified interval of time. Unfortunately, direct observations are very few even for dry land, not to mention the water areas of seas and oceans. As a result, numerical methods based upon more or less broad assumptions, and simplifications are now often used.

Direct evaluations of the intensities of deposition of atmospheric dust in various regions are presented in Table 2. Despite the fragmentary nature of the observations, one can see a pattern in the data reflecting more intensive dust deposition are still more weakly expressed in arid regions as compared to humid regions. The processes of eolian deposition in zones of ice cover in the Antarctic and Greenland and also in zones of alpine glaciers at temperate latitudes. This can be explained, on the one hand, by the significant distances of these areas from the major centers associated with the generation of terrigenous aerosol, and, on the other hand, by the great altitudes at which air masses contain low concentrations of mineral dust. Let us note that individual intensive "dust-falls" deposit as much dust as is deposited over a year under conditions usual for the regions mentioned [7]. This conclusion is confirmed by data presented in a report [36] according to which hurricanes in 1959 and 1969 transported 50 and 41 million tons of terrigenous material respectively to the water of the Azov Sea. This exceeds the average yearly supply due to the major sources of sedimentary material (fluvial discharge and coastal abrasion) by a factor of almost two.

It is also curious that perceptible quantities of eolian material fall on the northern coast of the Kola Peninsula [32]. It can be assumed that the material is local in its occurrence, forming in areas devoid of plant and snow cover. It is probable that the coatings of mineral dust occurring in variable amounts on the surface of arctic glaciers from Greenland to the Chukchi Sea are of precisely such an origin [10, 27, 30].

Somewhat surprising results were obtained when currents of mineral dust were measured in the Northern Atlantic; the currents there are comparable to currents on the continents, but the dust load of the air over the oceans is significantly lower than over dry land. Indications by the authors of [16] that the marine aerosol, consisting primarily of fine droplets of sea water, can markedly accelerate the settling of mineral dust deserve attention. Thus, the average effective rate of sedimentation of insoluble aerosol calculated according to the data of the authors mentioned is approximately 40 cm/sec; this is approximately 10-100 times higher than analogous rates for dry land [31]. In general, atmospheric humidity is a very effective agent for settling aerosols and must be taken into consideration when estimating scales of deposition of terrigenous material from the atmosphere to the surfaces of seas and oceans.

Two primary mechanisms of removing aerosols from the atmosphere exist: "dry" or gravitational settling (settling under the influence of gravity), and "humid" settling taking place as a result of the aerosol being washed out by atmospheric precipitation. The Stokes equation [4] is often used to estimate the rate of gravitational settling, but, under real conditions, turbulent and convective air currents exert a strong influence on the settling rate. Such components must be taken into consideration. The use of theoretical dependences to estimate the rate of dry settling requires knowledge of distribution functions for the number of particles with respect to size. As the investigations of recent years indicate, the size distribution of the particles of atmospheric aerosol can be well described by a log-normal function, while the superpositions of several normal-logarithmic functions can describe any complex natural distribution [19]. However, the coefficients which figure into these functions can differ markedly in different situations. It was also discovered that the size distribution of the aerosol mass, also exhibiting log normality, shows several modes. Two of them (0.1-0.2 and 2.8-2.9 μm) are characterized by significant invariance for different points of the globe and are present both for high and for low dust loads in the air. The third mode (20-35 μm) appears only under conditions of marked dust load [19, 53]. These data indicate that the choice of an average-mass value for the dimensions of atmospheric aerosol is an extremely complex problem (as is the case with many numerical estimates) which requires information on the distribution function over a wide range of sizes. When calculating the average rate of dry sedimentation, still another complication arises connected with the fact that the concentration of particles with dimensions exceeding 10-20 μm was not determined in the majority of studies. The contribution of these particles to the total mass of the aerosol is small, less still than their contribution to the total number of particles, but, because of their very high rate of sedimentation which is proportional

TABLE 3. Contribution of Various Fractions of Screened Aerosol (14°22' N, 26°24' W) to the Total Number of Particles N in the Total Mass m and the Average-Mass Velocity $\bar{v}_g$, %.

Parameter	Fraction, μm					
	0-2	2-4	4-8	8-16	16-32	32-64
N	78,3	15,4	5,6	0,56	0,11	0
m	1,9	9,9	28,9	23,1	36,3	0
$\bar{v}_g$	0,01	0,4	4,1	13,1	82,4	0

Explanation. For a density of particles amounting to 2.5 g/cm³, $\bar{v}_g = 8$ cm/sec.

to the square of the radius, these very coarse particles may be responsible for the primary flow of material sedimenting out. This is apparent from the determination of the average-mass rate of gravitational sedimentation:

$$\bar{v}_g = \sum m_i v_i / \sum m_i, \quad (1)$$

where m_i and v_i are, respectively, the mass and the rate of sedimentation of the i -th size fraction. The data of L. Johnson [49] on the granulometric composition of screened aerosol collected in the northern tropical Atlantic at a distance of 800 km from the shore are presented in Table 3. According to the calculations, 82.4% of the total flow was due to the coarsest (16-32 μm) fraction constituting 36.3% of the total mass and, in all, 0.11% of the total number of particles. Very coarse particles with dimensions of 10-100 μm are present at all altitudes in the troposphere (at least up to 5 km). It is necessary to keep this in mind during any calculations of the gravitational flows of terrigenous aerosol to the oceans [38]. Unfortunately, the density and material composition of the very coarse particles has gone practically unstudied, and, consequently, calculating their settling rate is very complicated. The unreliability of the calculations for intensity of dry sedimentation of mineral dust can increase still further because of difficulties connected with describing turbulent diffusion, convective air flows, and the interaction of the aerosol with the Earth's surface of a body of water [9]. In practice, therefore, there is a preference shown for a formal equation for a flow of dry sedimentation [31]:

$$F = v_{ef} N, \quad (2)$$

where v_{ef} is the effective rate of sedimentation which, in an implicit form, takes into consideration all of the processes affecting the rate of aerosol sedimentation, and N is the concentration of particles in the air.

In discussing the data presented in [16], we have already noted the anomalously high (40 cm/sec) values of v_{ef} which follow from the measurements presented in the report. The effective rate of dry sedimentation of aerosols in England amounted to approximately 0.35 cm/sec in [54]. For radioactive isotopes (²¹⁰Pb, ¹³¹I, ²¹⁴Pb, and ²¹⁴Bi), v_{ef} is usually within the range of 0.05-5 cm/sec [49]. Side by side with this, the average-mass rates for gravitational sedimentation of screened aerosol calculated according to the data presented in [49] yield values of the order of 10-50 cm/sec. The range of estimates for v_{ef} is therefore great (three orders of magnitude). From our point of view, this fact necessitates careful calculations of a different type, using both Stokes Law and the semiempirical equation (2), in order to find the scales of dry aerosol sedimentation.

The case is somewhat simpler with estimates of the quantity of aerosols removed from the atmosphere by precipitation. The existing data [31, 54] indicate that a substantial difference exists between the weight concentration of aerosols in the air (C_a , $\mu\text{g}/\text{m}^3$) and in water associated with atmospheric precipitation (C_w , $\mu\text{g}/\text{l}$). This dependence can be expressed by a simple relationship:

$$C_w/C_a \approx \text{const}, \quad (3)$$

where the constant ≈ 1000 (Table 4). By making use of this relationship and knowing the average concentration of aerosols in the air and the annual amount of precipitation, it is possible to approximately calculate the flow of material removed from the atmosphere as a

TABLE 4. Values for the Washing Factor (const) for Chemical Elements and Radioisotopes Contained in the Atmosphere

Element	England Vrainmairs [54]	USSR, ETS radioisotope [31]	USA, Chardon, Nebraska [60]	Alaska, Barrow [58]
Beryllium	—	910	—	—
Sodium	2900	—	—	240
Magnesium	—	—	—	330
Aluminum	620	—	850	1100
Phosphate	—	780—1200	—	—
Sulfur	—	650	—	—
Chlorine	2300	—	—	—
Calcium	—	—	—	2350
Scandium	710	—	—	—
Vanadium	510	—	—	170
Chromium	1200	—	—	—
Manganese	760	1400	1180	910
Iron	890	—	—	—
Cobalt	780	—	—	—
Copper	880	—	1070	—
Zinc	1050	—	810	100
Arsenic	640	—	—	—
Selenium	—	—	—	—
Bromine	620	—	—	—
Rubidium	640	—	—	—
Zircon	—	1200	—	—
Ruthenium	—	1400	—	—
Silver	—	—	670	—
Cadmium	—	—	700	160
Antimony	1150	780	—	—
Iodine	—	1800	—	—
Cesium	1050	1300	—	—
Barium	—	1200	—	—
Cerium	1400	1800	—	—
Lead	450	1300	140	—
Polonium	—	2200	—	—
Thorium	920	—	—	—
Mineral dust	—	4100	—	—

result of humid deposition. This method of determining the flows of a number of microelements from the atmosphere to the ocean has already been used by the author [29], and the more recent, complete data [62] generally confirms the estimates made above.

Unfortunately, there are no reliable experimental determinations of the ratio of humid to dry deposition of aerosols under the conditions of a marine atmosphere. For continental conditions, the ratio of humid to dry deposition depends primarily upon the total number of rainfalls, their intensities, and their durations. Usually, the concentration of admixtures, including aerosols, decrease in the air with an increase in the amount of precipitation falling [31]:

$$N_h = N_0 \exp(-bh), \quad (4)$$

where N_0 and N_h are the initial admixture concentration and the concentration after h precipitations respectively; b is a proportionality coefficient depending upon the type and character of the atmospheric precipitation. Thus, in the Elbrus region for example, b equals 0.14 mm^{-1} for snow and 0.59 mm^{-1} for rain [8].

By knowing the average concentration of aerosols during dry periods and also the average duration, intensity, and character of the precipitations, it is theoretically possible to use equation (4) to estimate the mass of aerosols removed from the atmosphere over the course of a year as a result of humid deposition and to calculate the mass of dry dust settlements for a known average rate of dry deposition. A comparison of these two values would allow one to estimate the ratio of humid to dry deposition for one or another region; however, such an approach would be impractical because of the dearth of necessary hydrometeorological information (especially for the water areas of seas and oceans). What is most expedient for finding the portion associated with dry deposition, therefore, is a search of semiempirical dependences using average yearly values for total precipitation (the data for such values exist in numerous handbooks). It is clear from qualitative considerations that the portion associated with dry deposition α should strive to zero for an increase in the average yearly amount of precipitation, i.e., $\alpha \rightarrow 1$ for $h \rightarrow 0$ and $\alpha \rightarrow 0$ for $h \rightarrow \infty$. It is apparent that a function of the type

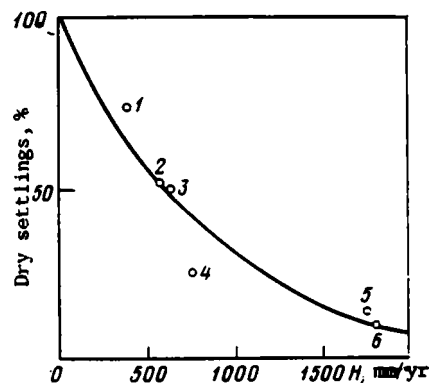


Fig. 1. Dependence of the portion of dry settlements upon the average yearly amount of atmosphere precipitations [12, 31, 37, 54] 1) Tashkent; 2) Moscow; 3) Paris; 4) Belgium; 5) Tokyo; 6) Vrainmairs (Great Britain).

TABLE 5. Information on the Major Regions of Eolian Accumulation over the Ocean [6] and the Contribution of the "Sea of Darkness" to the Total Eolian Accumulation

Regions of accumulation	Area of occurrence of dry dust clouds with various extents of recurrence, million km ²		
	25-35% (27 days)	15-25% (18 days)	10-15% (11 days)
Regions of winter accumulation			
"Sea of Darkness"	0,3	1,1	3,3
Waters washing up against Southwestern Africa	—	—	0,2
Waters washing up against South American coast	—	—	0,3
Regions of summer accumulation			
"Sea of Darkness"	—	0,3	0,7
Red and Arabian Seas	1,0	1,4	1,1
Waters washing up against Southwestern Africa	—	—	0,5
Waters washing up against the coast of South America	—	—	0,2
Waters washing up against arid regions of the western coasts of Mexico and the USA	—	0,3	0,7
Western portion of the Mediterranean Sea	—	—	0,6

Explanation. The indicator of the scales of eolian accumulation in the regions enumerated is the product of the number of days with dust clouds times their distribution, millions of km²; 1) 76.3 for the "Sea of Darkness"; 174.5 for all regions. The portion of the "Sea of Darkness" within the total eolian accumulation amounts to 43.7%.

$$\alpha = \frac{1}{1 + \beta h} \quad (5)$$

satisfies this condition. Actually, as is evident from figures constructed on the basis of existing information on the dry-deposition fraction of radioactive aerosols in localities with different average yearly amounts of precipitation [12, 31, 37, 54], Eq. (5) correctly gives the type of dependence of α upon h that allows one to make a rough estimate of ratio of dry to humid deposition of aerosols, including ratios for the water areas of seas and oceans, according to the known average annual amount of atmospheric precipitation.

Scales of Supply of Terrigenous Aerosol to the Oceans

It follows from the preceding discussion that the usually conducted estimates of the supply of terrigenous material to the oceans based upon calculations of the rate of gravitational settling are extremely unreliable. Therefore, we attempted to carry out similar estimates by several other routes, individually taking into consideration the background precipitation and periodic dust outbreaks from the primary source regions of terrigenous aerosol. As follows from the data presented in Table 1, the average background concentration of terrigenous aerosol amounts to approximately $1.5 \pm 0.5 \mu\text{g}/\text{m}^3$ and the average yearly amount of atmospheric precipitation over the ocean is 900 mm [35], which, when using relationship (3), gives a concentration of mineral dust in the precipitation equal to approximately $1.5 \pm 0.5 \mu\text{g}/\text{liter}$ and a flow of humid deposition equal to $1.35 \pm 0.45 \text{ g}/\text{m}^2 \cdot \text{yr}$ or 490 million tons/

year for the entire ocean. If the dependence of the fraction of dry dust settlements upon the yearly number of precipitations is extended to cover oceanic conditions (see Fig. 1), then the fraction of dry settlements for a 900-mm quantity of deposition will amount to approximately 35% of the total or 54% as much as the humid deposition. For an increase in the latter equal to 490 million tons, background deposition via dry settling amounts to approximately 265 million tons and the total background deposition amounts to 755 million tons.

In arriving at inferences concerning the quantity of mineral dust being supplied to the oceans as a result of dust outbreaks from the primary sources where terrigenous aerosols are generated, we profited from the data of L. G. Bondarev [6], who calculated the product of the number of days of the year with dust hazes times the area of haze distribution in millions of km^2 (Table 5) for major regions with intense periodic dustiness. In general, this indicator equals 174.5 for the World Ocean and amounts to 76.3 or 43.7% for the "Sea of Darkness." Estimates of the quantity of dust transported* along with air currents exist which are in fairly good agreement with one another. Thus, this value amounts to 25-50 million tons/year according to the data presented in [21], while approximately 53 million tons/yr are transported across the 20° W meridian between $10-25^\circ$ N according to the data presented in [13]. Judging from the decrease in the concentration of dust to the west of this region [19, 21], more than 90% of the transported dust settles out during the course of the transport. Therefore, one can assume that approximately 50 millions tons of terrigenous aerosol associated with dust outbreaks settle within the "Sea of Darkness" and adjacent water areas. This value, as follows from Table 5, corresponds to 43.7% of the total for dust outbreaks from the centers where terrigenous aerosols are generated; hence, the total supply of mineral dust over the course of strong, above-background-level dust outbreaks amounts to approximately 114 million tons. Summing up all of the atmospheric deliveries of terrigenous aerosol, we finally obtain a value on the order of 870 million tons/yr.

The fluvial discharge of suspended matter was estimated at 18,500 million tons/yr on the whole [23]; at the same time the contribution of eolian material was estimated to be approximately 4.5%. However, 90% of the fluvial suspensions settle out in the shelf zone and at the beginning of the continental slope [24]. In all, approximately 1800-1900 million tons/yr penetrate to the pelagic zone. Since the pelagic zone occupies approximately 77% of the area of the entire ocean, the modulus of supply for fluvial terrigenous suspensions amounts to approximately $6.5-6.8 \text{ g/m}^2 \cdot \text{yr}$. This value is comparable with the flow of humid deposition in background regions (constituting approximately $1.35 \text{ g/m}^2 \cdot \text{yr}$ on an average for the entire pelagic zone) and should be somewhat higher (approximately $2 \text{ g/m}^2 \cdot \text{yr}$, perhaps) when taking into consideration the phenomena of dry settling. For the oceanic pelagic zone, terrigenous eolian material thus averages 20-30% of the mass of annual fluvial suspensions delivered there, but it is evident that the relative contribution of eolian material can be substantially higher for the central regions of the oceans and can probably exceed the yield from fluvial suspensions. This problem requires special consideration, however.

LITERATURE CITED

1. R. V. Abramov, "Dust in the atmosphere over the Atlantic Ocean," in: Conditions of Sedimentation in the Atlantic Ocean [in Russian], Nauka, Moscow (1971), pp. 7-30.
2. I. A. Aleksina, "Toward a characterization of the eolian material of the Eastern coast of the Middle Caspian," Dokl. Akad. Nauk SSSR, 127, No. 2, 427-430 (1959).
3. B. A. Appolov, "The influence of eolian accumulation on the shoaling of the northern portion of the Caspian Sea," Izv. Tsentr. Gidrometeorol., Byuro, No. 2, 273-275 (1973).
4. S. Batchelor and R. Charlson, Introduction to the Chemistry of the Atmosphere [Russian translation], Mir, Moscow (1977).
5. L. S. Berg, Climate and Life [in Russian], Geografiz, Moscow (1947).
6. L. G. Bondarev, Perpetual Motion [in Russian], Mysl', Moscow (1974).
7. S. V. Bruevich and M. P. Gudkov, "Atmospheric dust over the Caspian Sea (with respect to marine sediment formation)," Izv. Akad. Nauk SSSR, No. 4, 18-28 (1954).
8. I. I. Burtsev, "The washing of artificial radioactive aerosols from the atmosphere by precipitation," in: Radioactive Isotopes in the Atmosphere and Their Use in Meteorology [in Russian], Atomizdat, Moscow (1965).

*Transported but not deposited! These estimates are not associated with an assumption of one or another rate of gravitational sedimentation, but are based upon physical observations.

9. N. L. Byzova and K. P. Makhon'ko, "The interaction of aerosols with the underlying surface," *Izv. Akad. Nauk SSSR, Fiz. Atm. Okeana*, 4, No. 9, 1000-1003 (1968).
10. V. I. Vlodavets, "Remarks concerning drifted mineral sediment on glaciers," *Tr. Ark-ticheskova Inst.*, 33, 79-85 (1936).
11. Al. A. Grigor'ev and V. B. Lipatov, "Distribution of dust contaminants in the Aral region according to observations from space," *Izv. Akad. Nauk SSSR, Ser. Geogr.*, No. 4, 73-77 (1983).
12. G. V. Dmitrieva, "The problem of 'dry' fall-out of radioactive fission products on the Earth's surface," in: *Investigations into Self-Cleaning Atmospheric Processes Removing Radioactive Isotopes* [in Russian], Mintis, Vilnius (1968), pp. 173-179.
13. E. M. Emel'aynov and L. V. Kool', "Transport of eolian dust and its role in the processes of sediment formation in the Atlantic Ocean," *Litol. Polezn. Iskop.*, 2, 3-15 (1979).
14. V. N. Zhivago, "Distribution of eolian suspension over the central and northern regions of the Indian Ocean," in: *Hydrophysical and Hydrooptical Investigations in the Indian Ocean* [in Russian], Nauka, Moscow (1975), pp. 200-213.
15. V. N. Zhivago and Yu. A. Bogdanov, "Eolian suspension over the Atlantic and Pacific Oceans," in: *Hydrophysical and Hydrooptical Investigations in the Atlantic and Pacific Oceans* [in Russian], Nauka, Moscow (1974), pp. 259-279.
16. T. A. Zhuravel', V. I. Medinets, and L. P. Fetisov, "Determination of the parameters associated with the removal of aerosols from the near-water atmosphere," *Tr. Gos. Okeanogr. Inst.*, No. 170, 94-97 (1983).
17. V. L. Zverev, A. I. Spiridonov, and V. M. Shvets, *Geokhimiya*, No. 5, 765-771 (1976).
18. K. Ya. Kondrat'ev, Al. A. Grigor'ev, O. M. Pokrovskii, and E. V. Shalina, *Remote Sensing of Atmospheric Aerosol from Space* [in Russian], Gidrometeoizdat, Leningrad (1983).
19. K. Ya. Kondrat'ev and D. V. Pozdnyakov, *Aerosol Models of the Atmosphere* [in Russian], Nauka, Moscow (1981).
20. V. M. Kotlyakov and F. G. Gordienko, *Isotopic and Geochemical Glaciology* [in Russian], Gidrometeoizdat, Leningrad (1982).
21. Zh. Kude-Gossen and P. Ron'on, "Dust of the Sahara," *Science and Life*, No. 2, 80-86 (1985).
22. R. D. Kedl, "Suspended particles in the lower atmosphere," in: *The Chemistry of the Lower Atmosphere* [Russian translation], Mir, Moscow (1986), pp. 90-154.
23. A. P. Lisitsyn, *Sediment Formation in the Oceans* [in Russian], Nauka, Moscow (1974).
24. A. P. Lisitsyn, *Processes of Oceanic Sedimentation* [in Russian], Nauka, Moscow (1978).
25. K. P. Makhon'ko and F. A. Rabotnova, "Concentration of mineral dust in the atmosphere over the territory of the USSR," *Meteorol. Gidrol.*, No. 1, 61-65 (1981).
26. A. Z. Miklishanskii, Yu. V. Yakovlev, B. V. Savel'ev, and A. P. Zuev, "Make-up and chemical composition of the mineral phase in cores of the ice cover of the central regions of Antarctica," *Geokhimiya*, No. 2, 286-293.
27. F. Nansen, *Environments of the Common Seals and Polar Bears* [in Russian], Collected Works, Glavsevmorputi (1939), pp. 17-458.
28. F. P. Savarenskii, "Atmospheric dust falling with snow from the 8th to the 9th of April. 1907 in the vicinity of Mt. Kaluga (1911)," *Selected Works*, Akad. Nauk SSSR (1950), pp. 19-20.
29. V. S. Savenko, V. V. Anikiev, and G. M. Kolesov, "Entry of toxic elements to marine water from the atmosphere," *Material from the 5th All-Union Symposium*, Tallin, November 18-21, (1975, *Inst. Okeanol. Akad. Nauk SSSR*) (1975), pp. 135-139.
30. G. U. Sverdrup, "Voyage on the 'Mod' in the waters of the Laptev and Eastern Siberian Seas," *Material of the Commission for the Study of the Yakutsk ASSR*, No. 30 (1930).
31. B. I. Styro, V. Yu. Luyanas, and K. K. Shipauskas, *Radioactivity of the Atmosphere and Meteorology* [in Russian], Mintis, Vilnius (1975).
32. G. A. Tarasov, "In influence of eolian drift on sediment formation in the Barents Sea," *Dokl. Akad. Nauk SSSR*, 244, No. 3, 728-730 (1979).
33. M. V. Fedosov, "Eolian accumulation in the northern Caspian," *Dokl. Akad. Nauk SSSR*, 75, No. 6, 847-849 (1950).
34. V. Fett, *Atmospheric Dust* [Russian translation], IL, Moscow (1961).
35. R. Khron, *Marine Chemistry* [Russian translation], Mir, Moscow (1972).
36. Yu. P. Khrustalev and V. I. Fedyunina, "Role of the eolian factor in modern sediment accumulation in the Azov Sea," *Dokl. Akad. Nauk SSSR*, 244, No. 2, 434-436 (1975).
37. A. É. Shem'i-zade, "Dry fall-out of the products of nuclear testing," *At. Energ.*, 24, No. 5, 474-475 (1968).

38. M. S. Él'mesov and G. V. Stepanov, "Results of investigations of the content of giant and supergiant particles in the atmosphere," *Izv. Akad. Nauk SSSR, Fiz. Atmos. Okeana*, 15, No. 5, 639-647 (1979).
39. Kh. Yunge, *Chemical Composition and Radioactivity of the Atmosphere* [Russian translation], Mir, Moscow (1965).
40. S. R. Aston, R. Chester, L. R. Johnson, and R. C. Padgham, "Eolian dust from the lower atmosphere of the eastern Atlantic and Indian oceans, China Sea and Sea of Japan, *Marine Geol.*, 14, No. 1, 15-28 (1973).
41. P. E. Biscaye, R. Chesselet, and J. M. Prospero, "Rb-Sr, $^{87}\text{Sr}/^{86}\text{Sr}$ isotope system as an index of provenance of continental dust in the open Atlantic Ocean," *J. Rech. Atmo.*, 8, Nos. 3-4, 819-829 (1974).
42. R. Chester, H. Elderfield, and J. J. Griffin, "Dust transport in the Northeast and Southeast winds in the Atlantic Ocean," *Nature*, 233, No. 5230, 474-476 (1971).
43. R. Chester and L. G. Johnson, "Atmospheric dust collected off the west African coast," *Nature*, 299, No. 5280, 105-107 (1971).
44. R. Chester and L. G. Johnson, "Atmospheric dust collected off the Atlantic coasts of North Africa and the Iberian Peninsula," *Marine Geol.*, 11, No. 4, 251-260 (1976).
45. A. C. Delany, D. W. Parkin, J. J. Griffin, et al., "Airborne dust collected at Barbados," *Geochim. Cosmochim. Acta*, 31, No. 5, 885-909 (1967).
46. W. S. Fergusson, J. J. Griffin, and E. D. Goldberg, "Atmospheric dust from the North Pacific - a short note on a long-range eolian transport," *J. Geophys. Res.*, 75, No. 6, 1137-1139 (1970).
47. E. D. Goldberg and J. J. Griffin, "The sediments of the northern Indian Ocean," *Deep-Sea Res.*, 17, No. 3, 513-532 (1970).
48. C. U. Hammer, "Past volcanism revealed by Greenland ice sheet impurities," *Nature*, 270, No. 5637, 482-486 (1977).
49. L. G. Johnson, "Particle-size fractionation of eolian dusts during transport and sampling," *Marine Geol.*, 21, No. 1, 17-21 (1976).
50. C. E. Junge, "Our knowledge of the physicochemistry of aerosols in the undisturbed marine environment," *J. Geophys. Res.*, 77, No. 27, 5183-5200 (1972).
51. D. W. Parkin, A. C. Delany, and A. C. Delany, "A search for airborne cosmic dust on Barbados," *Geochim. Cosmochim. Acta*, 31, No. 8, 1311-1320 (1967).
52. D. W. Parkin, D. R. Phillips, R. A. L. Sullivan, and L. Johnson, "Airborne dust collection over the North Atlantic," *J. Geophys. Res.*, 75, No. 9, 1782-1793 (1970).
53. E. M. Patterson and D. A. Gillette, "Commonalities in measured size distribution for aerosols having a soil-derived component," *J. Geophys. Res.*, 82, No. 15, 2074-2082 (1977).
54. D. H. Peirson, A. Cawse, L. Salmon, and R. S. Cambray, "Trace elements in the atmospheric environment," *Nature*, 241, No. 5387, 252-256 (1973).
55. J. M. Prospero, "Atmospheric dust studies on Barbados," *Bull. Am. Meteorol. Soc.*, 49, No. 6, 645-652 (1968).
56. J. M. Prospero, "Mineral and sea salt aerosol concentration in various ocean regions," *J. Geophys. Res.*, 84, No. C2, 725-731 (1979).
57. J. M. Prospero and E. Bonatti, "Continental dust in the atmosphere of the eastern equatorial Pacific," *J. Geophys. Res.*, 74, No. 13, 3362-3371 (1969).
58. K. A. Rahn and R. J. McCaffrey, "Compositional differences between Arctic aerosol and snow," *Nature*, 280, No. 5722, 479-480 (1979).
59. D. L. Savoie and J. M. Prospero, "Aerosol concentration statistics for the northern tropical Atlantic," *J. Geophys. Res.*, 82, No. 37, 5954-5964 (1977).
60. A. W. Struempfer, "Aerosol metal relationships in air and precipitation," *Environment Internat.*, 2, No. 1, 63-65 (1979).
61. L. Tomadin, R. Lenaz, V. Landuzzi, et al., "Wind-blown dusts over the Central Mediterranean," *Oceanol. Acta*, 7, No. 1, 13-23 (1984).
62. M. Waldichuk, "Exchange of substances between the atmosphere and the oceans," 3rd Internat. Sympos. on Integrated Global Monitoring of the State of the Biosphere, Tashkent, USSR, October 13-20, (1985), Preprint.
63. H. L. Windom, "Atmospheric dust records in permanent snowfields: implications to marine sedimentation," *Bull. Geol. Soc. Am.*, 80, No. 5, 761-782 (1969).

Results are generalized which were obtained during the structural and crystal-chemistry study of globular, dioctahedral, 2:1 layered silicates, represented in deposits studied (of varying age) by low-charge micas — glauconite, Al-glauconite, and illite and their structural varieties (hydromicas and mixed-layer formations). Of these minerals, three structurally isomorphous series are distinguished: glauconite → glauconite-smectite, Al-glauconite → Al-glauconite-smectite, and illite → illite-smectite, representatives of which are differentiated on the basis of crystal-chemistry features and stratigraphic area of limitation.

The purpose of this article is to state the results obtained in crystal-chemistry structural studies of globular varieties of dioctahedral 2:1 layered silicates, represented by glauconite, Al-glauconite (Fe-illite), and illite, as well as their structural varieties (hydromicas and mixed-layer minerals). These silicates are limited to marine deposits and various lithological type and age, from Lower Riphean to Lower Cambrian inclusive in the USSR, as well as in the Paleogene in Syria. In terrigenous rocks (sandstones and siltstones), occasionally interbedded with clay rocks, the globules studied were encountered by T. A. Ivanovskaya in sections of the Upper Riphean in the southern Urals, the Upper Proterozoic of eastern Siberia, and the Lower Cambrian of northern Estonia. In dolomites, they were selected by the same author from the Ust'yudom suite of the Wendian and in limestones from the varicolored suite of the Lower Cambrian. In addition, material was analyzed from marls of Paleogene age (Paleocene and Eocene) in Syria (the collection of V. A. Krasheninikov). A brief description of the rocks in the sections studied and an analysis of their epigenetic (katagenetic) changes were provided in [7]; these questions will be considered in more detail in a separate publication.

The article presented supplements on the crystal chemical data already known from the literature on globular layered silicates [1, 8, 9, 14, 15]. In particular, this involves globules of Precambrian age, composed of illitic and Al-glauconitic minerals, which, in comparison with true (iron) glauconite, have so far been studied very poorly. The crystal-chemical structural characteristics of layered silicates, partially presented previously [3-7, 10], are based on chemical, diffraction (x-ray and electronographic), and IR spectroscopic investigations performed at the Institute of Geology, USSR Academy of Sciences.

The crystal-chemical formulas of the minerals studied are presented in Tables 1 and 2, and their diffraction characteristics are in Tables 3 and 4. As seen from the data in these tables, among the samples studied with different compositions which are the subject of classification [8, 11], we separate the nonswelling minerals which contain <10% smectite layers, as well as hydromicas and mixed-layer formations (with 10-20% and >20% smectite layers, respectively). Hydromicas occupy a predominant place in the assemblage studied (25 samples out of 60). Nonswelling and mixed-layer minerals are encountered in lesser amount (20 and 15 samples, respectively). The most complete crystal-chemical characteristics are presented for the hydromicas and mixed-layer formations. As for the nonswelling minerals, detailed characteristics were obtained for only four of the samples. In the remaining samples, these minerals were either insufficient for study due to the quantity of material (five samples from the Precambrian of Siberia), or they turned out to be one of the components in globules of two-phase mica composition (11 samples from the Lower Cambrian of Siberia).

The International Committee on Nomenclature (ICN) defined the crystal-chemical parameters of glauconite [12]. It is a dioctahedral high-iron-content mica mineral, containing

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TABLE 1. Crystal Chemical Formulas for Minerals of Paleogene Age

Sample No.	Size, mm	Density, g/cm ³	Cations										Charge			Level of iron content
			tetrahedral		octahedral					interlayer						
			Si	Al	Fe ³⁺	Al	Fe ²⁺	Mg	Σ	K	Na	Ca	tetra- hedral	octa- hedral	inter- layer	
1	0,2—0,1	2,45—2,7	3,68	0,32	0,82	0,54	0,06	0,68	2,10	0,60	0,03	0,07	15,68	5,56	0,77	0,60
2	0,315—0,16	2,55—2,65	3,71	0,29	0,93	0,43	0,05	0,66	2,07	0,59	0,02	0,08	15,71	5,50	0,77	0,68
3	0,315—0,2	2,5—2,6	3,68	0,32	1,07	0,26	0,03	0,81	2,17	0,54	0,03	0,03	15,68	5,67	0,63	0,80
4	0,2—0,1	2,6—2,7	3,75	0,25	0,81	0,55	0,06	0,64	2,06	0,68	0,02	0,02	15,75	5,48	0,74	0,60
5A	0,315—0,16	2,55—2,6	3,69	0,31	0,91	0,54	0,03	0,55	2,03	0,61	0,01	0,08	15,69	5,51	0,78	0,63
5B	0,315—0,16	2,65—2,7	3,71	0,29	0,94	0,43	0,06	0,61	2,04	0,64	0,02	0,10	15,71	5,45	0,86	0,69
5C	0,315—0,16	2,75—2,8	3,69	0,34	0,94	0,42	0,07	0,58	2,01	0,75	0,06	0,08	15,69	5,38	0,97	0,69
6A	0,315—0,2	2,45—2,5	3,75	0,25	0,69	0,74	0,02	0,58	2,03	0,46	0,04	0,12	15,75	5,49	0,74	0,48
6B	0,315—0,2	2,55—2,6	3,60	0,40	0,76	0,71	0,06	0,60	2,13	0,60	0,02	0,01	15,60	5,73	0,64	0,52
6C	0,315—0,2	2,7—2,75	3,68	0,32	0,83	0,52	0,07	0,58	2,00	0,71	0,03	0,11	15,68	5,35	0,96	0,61
7A	0,315—0,2	2,45—2,5	3,73	0,27	0,88	0,62	0,03	0,55	2,08	0,51	0,03	0,06	15,73	5,66	0,66	0,59
7B	0,315—0,2	2,5—2,55	3,70	0,30	0,87	0,59	0,03	0,54	2,03	0,55	0,03	0,10	15,70	5,52	0,78	0,60
7C	0,315—0,2	2,55—2,65	3,71	0,29	0,95	0,56	0,02	0,54	2,07	0,57	0,03	—	15,71	5,65	0,60	0,63
7D	0,315—0,2	2,7—2,75	3,70	0,30	0,93	0,44	0,07	0,53	1,97	0,71	0,03	0,11	15,70	5,31	0,96	0,68
8A	0,315—0,16	2,55—2,6	3,68	0,32	0,73	0,71	0,05	0,63	2,12	0,59	0,02	0,01	15,68	5,68	0,63	0,51
8B	0,315—0,16	2,6—2,65	3,75	0,25	0,85	0,60	0,03	0,48	1,96	0,67	0,01	0,08	15,75	5,37	0,84	0,59
9A	0,315—0,2	2,55—2,6	3,66	0,34	0,78	0,66	0,04	0,63	2,11	0,60	0,02	0,04	15,66	5,66	0,70	0,54
9B	0,315—0,2	2,6—2,65	3,73	0,27	0,92	0,55	0,03	0,57	2,07	0,56	0,01	0,06	15,73	5,61	0,69	0,63
9C	0,315—0,2	2,6—2,7	3,68	0,32	0,74	0,65	0,06	0,68	2,13	0,63	0,02	—	15,68	5,65	0,65	0,53
9D	0,315—0,2	2,65—2,75	3,71	0,29	0,93	0,50	0,04	0,56	2,03	0,65	0,01	0,07	15,71	5,49	0,80	0,65
10	0,2—0,1	2,55—2,6	3,69	0,31	1,01	0,53	0,01	0,49	2,04	0,56	0,01	0,06	15,69	5,62	0,69	0,66
11	0,315—0,16	2,55—2,6	3,76	0,24	0,97	0,46	0,02	0,58	2,03	0,57	0,03	0,08	15,76	5,49	0,76	0,68

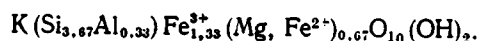
TABLE 2. Crystal Chemical Formulas for Minerals of Cambrian and Precambrian Age

Sample No.	Rock type	Grain size, mm	Grain density, g cm ³	Cations										Charge			Level of iron content	
				tetrahedral		octahedral				interlayer				tetra- hedral	octa- hedral	inter- lauer		
				Si	Al	Fe ²⁺	Al	Fe ³⁺	Mg	Σ	K	Na	Ca					
Lower Cambrian of northern Estonia and the Uchur-Maya region																		
1	Clays and siltstones	0,315-0,2	2,7-2,75	3,54	0,46	1,10	0,57	0,11	0,24	2,02	0,70	0,03	—	15,56	5,71	0,73	0,66	
2		0,315-0,2	2,7-2,75	3,57	0,43	1,10	0,57	0,08	0,25	2,01	0,69	0,03	—	15,57	5,7	0,72	0,66	
3		0,315-0,2	2,7-2,75	3,61	0,39	0,94	0,67	0,15	0,26	2,02	0,70	0,03	—	15,61	5,65	0,73	0,56	
4		0,2-0,1	2,7-2,75	3,47	0,53	1,20	0,44	0,12	0,32	2,03	0,63	0,01	0,04	15,47	5,8	0,75	0,73	
5		0,2-0,1	2,7-2,75	3,53	0,47	1,11	0,47	0,18	0,30	2,06	0,65	0,01	0,04	15,53	5,7	0,74	0,71	
6	Limestone	0,1-0,063	2,75-2,8	3,68	0,32	0,79	0,56	0,22	0,49	2,03	0,70	0,02	0,03	15,68	5,47	0,84	0,59	
7		0,16-0,1	2,75-2,85	3,59	0,41	0,73	0,76	0,20	0,37	2,06	0,78	0,01	—	15,59	5,61	0,79	0,49	
8		0,1-0,063	2,6-2,8	3,62	0,38	0,47	0,92	0,15	0,59	2,13	0,72	0,01	—	15,62	5,65	0,73	0,34	
Vendian and Upper Riphean in the southern Urals and the Uchur-Maya region																		
9	Dolomite	0,16-0,1	2,6-2,8	3,56	0,44	0,48	0,89	0,11	0,65	2,13	0,75	0,02	—	15,56	5,63	0,77	0,35	
10	Sandstone	0,4-0,2	2,55-2,61	3,59	0,41	0,29	1,44	0,04	0,25	2,02	0,60	0,02	0,01	15,59	5,77	0,64	0,17	
11	Siltstone	0,1-0,063	—	3,42	0,58	0,53	1,19	0,08	0,25	2,05	0,70	0,01	0,02	15,42	5,82	0,75	0,31	
12		0,1-0,063	—	3,58	0,42	0,37	1,31	0,10	0,23	2,01	0,66	0,01	0,02	15,58	5,70	0,71	0,22	
13		0,1-0,063	—	3,48	0,52	0,47	1,24	0,08	0,25	2,05	0,70	—	—	15,48	5,81	0,70	0,27	
14		0,1-0,063	—	3,44	0,56	0,48	1,16	0,13	0,23	2,06	0,73	0,01	0,03	15,44	5,76	0,80	0,29	
15		0,1-0,063	—	3,48	0,52	0,50	1,14	0,16	0,26	2,06	0,75	0,01	—	15,48	5,76	0,76	0,30	
16		0,1-0,063	—	3,38	0,62	0,39	1,29	0,14	0,25	2,07	0,78	0,01	—	15,38	5,82	0,79	0,23	
17		0,1-0,063	2,7-2,75	3,50	0,50	0,41	1,18	0,08	0,39	2,06	0,75	0,01	—	15,5	5,71	0,76	0,26	
18		Shale	0,315-0,2	2,6-2,7	3,54	0,46	0,24	1,24	0,12	0,44	2,04	0,74	0,01	0,06	15,54	5,56	0,87	0,16
19		Siltstone	0,315-0,2	2,65-2,7	2,64	0,36	0,16	1,34	0,11	0,40	2,01	0,75	0,01	0,02	15,64	5,52	0,80	0,19
20			0,1-0,063	2,6-2,7	3,53	0,47	0,31	1,34	0,14	0,26	2,05	0,63	0,03	0,03	15,53	5,75	0,72	0,19
Middle Riphean of the Uchur-Maya region																		
21	Sandstone	0,63-0,315	2,6-2,65	3,59	0,41	0,78	0,84	0,08	0,38	2,06	0,62	0,02	0,01	15,59	5,78	0,67	0,48	
22	Siltstone	0,315-0,2	2,55-2,65	3,63	0,37	0,67	0,90	0,13	0,37	2,07	0,59	0,02	0,03	15,63	5,71	0,63	0,42	
23		0,315-0,2	2,6-2,7	3,68	0,32	0,71	0,87	0,16	0,30	2,04	0,61	0,03	0,02	15,68	5,66	0,68	0,45	
24		0,315-0,2	2,6-2,7	3,54	0,46	0,52	1,17	0,04	0,27	2,00	0,66	0,02	0,03	15,54	5,69	0,74	0,31	
25	Sandstone	0,16-0,1	2,65-2,75	3,44	0,56	0,40	1,27	0,13	0,24	2,04	0,74	0,01	0,02	15,44	5,74	0,79	0,24	
26		0,4-0,2	2,7-2,8	3,72	0,28	0,32	0,97	0,15	0,67	2,11	0,77	0,01	—	15,72	5,51	0,78	0,25	
Lower Riphean of the Uchur-Maya region																		
27	Sandstone	0,4-0,315	2,75-2,8	3,75	0,25	0,58	0,81	0,10	0,48	1,97	0,84	0,02	0,03	15,73	5,33	0,92	0,42	

TABLE 3. X-Ray Data for Minerals of Paleogene Age

Sample number	$d(001), \text{\AA}$		Swelling layers, %	$d(060), \text{\AA}$ (polytype)
	natural	saturated		
1	10,30	9,72	25-30	—
2	10,30	9,63	35-40	—
3	10,40	9,83	15-20	—
4	10,00	9,78	20-25	—
5A	—	—	—	1,510 (1M)
5B	9,94	9,74	25-30	—
5C	—	—	—	1,512 (1M)
6B	10,33	9,78	20-25	—
7C	10,28	9,74	25-30	—
8A	10,05	9,80	15-20	1,512 (1M)
9A	10,45	9,72	25-30	1,512 (1M)
9C	10,07	9,78	20-25	—
10	10,28	9,68	30-35	1,512 (1M)
11	10,50	9,76	20-25	—

no swelling layers, with the ideal formula of



The parameter b of the mineral's elementary lattice is greater than 9.06 Å. Somewhat later, the ICN settled upon lowering the limits for potassium content in the glauconite structure to 0.9 formula units (f.u.) [13].

Based on analysis of data in the literature on glauconite [9, 15], it is evident that as a practical matter, the content of mixed-layer potassium cations in this mineral is almost always less than 0.9 f.u. This is true, in particular, of those samples which served the ICN [14] as a basis for separating only the ideal formula presented. A wide range of isomorphous replacements in octahedral and tetrahedral positions is characteristic of the mineral. In particular, it may be represented by both high-iron and high-aluminum-content varieties, which is not mentioned in the ICN data, and which do not correspond to glauconite proper, based on the Fe^{3+} content in the structure.

For low-charge, nonswelling Al-bearing mica minerals (K 0.6-0.8 f.u.), in contrast to true nonswelling high-charge (K 0.9-1.0 f.u.) Al, Mg-dioctahedral micas (muscovite, phengite leucophyllite), the ICN proposed using the term "illite" [13]. The committee emphasized that such a name ought to be given to the mineral on the basis of crystal-chemical and not genetic features, which for illite consist of the following. For a general layer charge in the mineral of less than 0.8 f.u., a phengitic component is present in its composition. Here a reduction in the layer charge in illite (by 0.2-0.4 f.u.) occurs due to an increase in the degree of replacement of Al by Si in the tetrahedra and the reduction in concentration of bivalent cations in the octahedra. The ideal formula for illite has the form



The minerals the authors studied were low-charge (potassium content does not exceed 0.8 f.u.). This refers not only to the hydromicas and mixed-layer minerals, but also to the non swelling (mica) varieties, which can belong to low-charge micas. In the entire assemblage studied, a rather wide range of Fe^{3+} and Al oscillations is observed in the octahedral positions of the 2:1 layers of the minerals, in f.u.: in low-charge micas, Fe^{3+} 0.16-0.79*, Al 0.56-1.34; in hydromicas, Fe^{3+} 0.24-1.20, Al 0.26-1.44; in mixed-layer formations, Fe^{3+} 0.31-1.01, Al 0.26-1.44. This also leads to a change on the level of iron content (n),[†] which was in the range of 0.16-0.80 in the samples studied. Of the micas, it is possible to distinguish glauconite ($\text{Fe}^{3+} > \text{Al}$, $n > 0.50$) and illite ($\text{Al} \gg \text{Fe}^{3+}$, $n < 0.25$) on the basis of composition and level of iron content, while the intermediate varieties belong to Al-glauconite[‡] ($\text{Al} \geq \text{Fe}^{3+}$, n 0.25-0.50). Such a distinction bears a somewhat arbitrary

*Higher Fe^{3+} contents in the octahedral grids of 2:1 layers are peculiar to other samples of mica studied, judging from the elementary lattice parameter b equal to 9.06-9.10 Å, but, as has already been pointed out, crystal-chemical formulas are lacking for these.

†The level of iron content is defined by the ratio $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Al})$.

‡Al-glauconite is similar to Fe-illite on the basis of crystal-chemical features [1], but the parameters of these minerals have still not been defined by the ICN.

TABLE 4. Elementary Lattice Parameters and X-Ray Data for Minerals of Lower Cambrian and Precambrian Age

Sample No.	a	b	c	β , deg	$-c \cos \beta/a$	d (001), Å		Swelling layers, %
	Å					natural	saturated	
Lower Cambrian of northern Estonia, and the Uchur-Maya region								
1	—	—	—	—	—	10,3	9,82	15—20
2	5,25	9,09	10,13	101,0	0,368	10,4	10,03	15—20
3	5,25	9,09	10,13	101,0	0,368	10,3	9,82	15—20
4	5,24	9,08	10,12	101,0	0,368	10,5	9,86	10—15
5	—	—	—	—	—	10,3	9,89	10—15
6	5,23	9,07	10,15	101,0	0,370	10,0	9,9	5—10
7	—	—	—	—	—	10,0	9,9	5—10
8	—	—	—	—	—	10,18	9,78	20—25
Vendian and Upper Riphean of the southern Ural and the Uchur-Maya region								
9	5,21	9,02	10,17	101,2	0,379	9,94	9,87	10—15
10	5,20	9,01	10,26	101,6	0,393	10,5	11; 9,61	15—20
11	5,21	9,01	10,3	101,2	0,383	10,25	9,72	25—30
12	5,21	9,02	10,25	101,1	0,379	10,16	9,8	15—20
13	5,21	9,01	10,25	101,15	0,379	10,23	9,8	15—20
14	5,21	9,01	10,25	101,3	0,379	10,23	9,8	15—20
15	5,21	9,01	10,3	101,2	0,383	10,04	9,82	15—20
17	5,22	9,04	10,26	101,2	0,381	10,28	9,72	25—30
18	5,23	9,02	10,12	101,2	0,375	10,24	9,88	10—15
19	5,22	9,03	10,13	101,2	0,377	10,13	9,97	<5
20	5,22	9,04	10,23	101,2	0,379	10,28	9,61	>30
Middle Riphean of the Uchur-Maya region								
21	5,24	9,06	10,17	101	0,370	10,28	9,82	15—20
22	5,22	9,03	10,13	101,2	0,375	10,28	9,82	15—20
23	5,23	9,06	10,3	101	0,375	10,53	11,05; 9,61	15—20
24	5,23	9,05	10,21	101,2	0,378	10,4	9,8	15—20
25	5,22	9,05	10,17	101,2	0,377	10,16	9,75	20—25
26	5,23	9,05	10,06	100,66	0,356	10,04	9,96	<5
Lower Riphean of the Uchur-Maya region								
27	5,23	9,06	10,17	101,0	0,371	10,05	9,83	15—20
28	5,22	9,05	10,0	101	—	9,93	9,95	<5

Note. In samples 21-23, the polytype is 1Md-1M; in the remaining ones, it is 1M, except for samp. 28, which is 1Md.

character, especially in the boundary regions, but on the whole for glauconite and illite, they agree with the data presented in [10].

Isomorphous replacements of $\text{Fe}^{3+} \rightleftharpoons \text{Al}$ in octahedral positions are observed in glauconite, its Al variety, and illite. Thus, the Fe^{3+} content decreases from 0.79 to 0.15 f.u. from glauconite through Al-glauconite to illite, while Al content increases from 0.56 to 1.34 f.u. This allows us to combine the minerals described into a single isomorphous series, as was done in [1, 7],* and for each of these in turn to distinguish the following structural series: mica - hydromica - mixed-layer formation. In these three structural-isomorph series, the limits for octahedral oscillations and iron content level are as follows, in f.u.: 1) glauconite-glauconite-smectite (Fe^{3+} 1.20-0.73, Al 0.26-0.71, $n > 0.5$); 2) Al-glauconite-glauconite-smectite (Fe^{3+} 0.76-0.41, Al 0.76-1.24, n 0.5-0.25); 3) illite-illite-smectite (Fe^{3+} 0.40-0.16, Al 1.24-1.44, $n < 0.25$). Tables 1 and 2 and Fig. 1 serve as an illustration of what has been stated, in which the relationship is considered between the level of iron content in the minerals and their potassium content.

Analyzing the potassium content, the following features may be noted. In all the minerals studied, this cation predominates in interlayer positions. Its content in low-charge micas of different compositions varies insignificantly (0.70-0.78), while in hydromicas and mixed-layer formations, it varies over a broad range (0.54-0.78, in one case up to 0.84). Here, the lowest amount of potassium (<0.6 f.u.) is more characteristic of glauconitic

*In [7], the terms "Fe-phengite" and "Al-glauconite" are satisfactory for the Al-bearing mica minerals studied. From the viewpoint of crystal-chemical features, it is more correct to use the term "illite" than "Fe-phengite,"

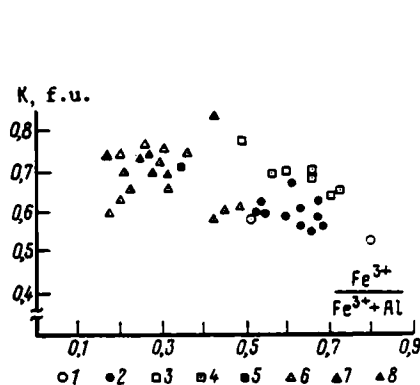


Fig. 1

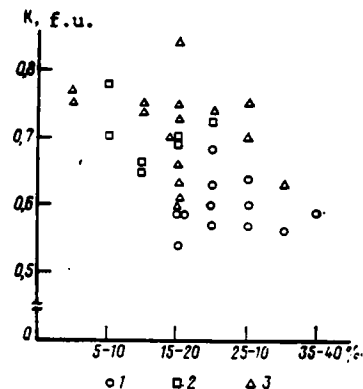


Fig. 2

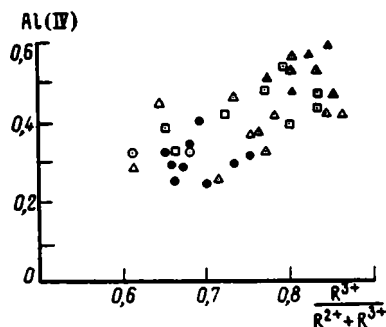


Fig. 3

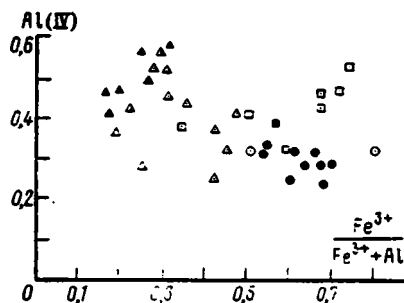


Fig. 4

Fig. 1. Relationship between potassium content and level of iron content in the minerals studied. 1-2) Paleogene samples (1: hydromicas, 2: mixed-layer formations), 3-5) Lower Cambrian samples (3: micas, 4: hydromicas, 5: mixed-layer formations), 6-8) Precambrian samples (6: micas, 7: hydromicas, 8: mixed-layer formations).

Fig. 2. Relationship between potassium content in the minerals studied and the share of swelling layers in their structure. Samples: 1: Paleogene; 2: Lower Cambrian; 3: Precambrian.

Fig. 3. Value of tetrahedral charge as a function of the ratio of bi- and trivalent cations in octahedral grids. See Fig. 1 for arbitrary designations.

Fig. 4. Value of tetrahedral charge as a function of level of iron content. See Fig. 1 for arbitrary designations.

hydromicas and mixed-layer glauconite-smectite minerals from the Paleogene of Syria, but sometimes it is also noted in Precambrian illite-smectite formations.

A distinct relationship is not observed between the level of the mineral's iron content and the concentration of potassium in its structure in the assemblage studied. One may only note an indistinctly expressed tendency toward reduction in potassium content with an increase in the level of iron content in the minerals. This, however, is only noted thanks to the presence of low-potassium Paleogene samples (see Fig. 1).

The relationship, described in the literature, of a reduction in the proportion of smectite layers with an increase in potassium content is not traceable in the Precambrian and Cambrian minerals studied. This relationship appears only upon exclusion from consideration of the Paleogene samples, which on the whole possess an elevated proportion of swelling layers and a reduced potassium content (Fig. 2).

As is seen from Fig. 2, in minerals with sufficiently high potassium content (≥ 0.7 f.u.), the swelling layers may be practically absent ($< 10\%$) or may reach significant proportions (up to 25-30% or higher). On the other hand, with the same content of swelling layers (15-20%), the amount of potassium in the structure may vary sharply (from 0.54-0.84 f.u.).

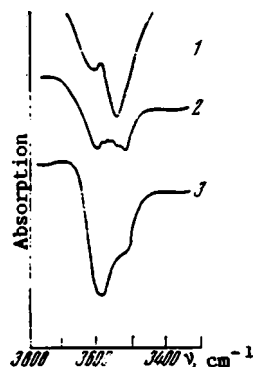


Fig. 5. IR spectra of minerals studied. Composition: 1) glauconitic, 2) Al-glauconitic, 3) illitic.

Such different degrees of mixed-layer content may be caused by the disorientation of sequential 2:1 layers in the mineral. In addition, the appearance of swelling layers is associated with uniformity in the distribution of the "large" K cations in the crystal volume, as well as with the presence of "small" Ca, Na, and Mg cations in its structure. Thus, after saturating sample 17, containing >30% swelling layers, with potassium cations in a 1N solution of K_2CO_3 , the potassium becomes the only interlayer cation, and practically all the swelling layers in the sample disappear (<5% are left).

In addition to the isovalent isomorphism $Fe^{3+} \rightleftharpoons Al$ in the samples studied, heterovalent isomorphism is rather widely observed in octahedral (Fe^{3+} , $Al \rightleftharpoons Mg$, Fe^{2+}) and tetrahedral ($Si^{4+} \rightleftharpoons Al^{3+}$) grids of the 2:1 layers (see Tables 1 and 2 and Fig. 3). As is evident from Fig. 3, the content of tetrahedral Al is clearly increased with a decrease in the concentration of bivalent cations in the octahedral grids, which confirms the different distributions of layer charge in the tetrahedral and octahedral grids. At the same time, such a clear relationship is not traced between the content of tetrahedral Al and the composition of trivalent cations. It is only noted in the entire collection of samples, but it disappears if the Paleogene data are excluded from consideration (Fig. 4).

Isomorphous replacements in the octahedral positions of 2:1 dioctahedral phyllosilicates finds its reflection in a change in the value of parameters in their elementary lattices. It is evident from diffraction data (see Tables 3 and 4) that the parameter b in the minerals studied varies from 9.01 to 9.10 Å in the transition from Al varieties to iron ones. In addition, if the parameter $-C \cos \beta/a$ in layered high-iron silicates (glauconite) has a value of 0.35-0.37, then in minerals of aluminum composition, its value increases to 0.39. This is evidence of a rather high degree of distortion in the polyhedra in the structure, associated with replacement in the octahedral positions of 2:1 layers by Fe^{3+} cations with large ionic radii for the "smaller" Al cations. Here, on oblique structure electronograms (OSE) of minerals with an illitic composition, a splitting of two pairs of reflections $20(\ell + 1)$, 13ℓ , 20ℓ , $13(\ell + 1)$ is observed in the second ellipse, while on the OSE's of glauconitic minerals, these splittings are practically absent. Changes in cation composition are also reflected in the distribution of intense reflections of the sixth and seventh ellipse, lying on the minor axis of the OSE [2]. In high-iron dioctahedral 2:1 layered silicates (glauconitic composition), the intensity of the reflection lying on the sixth ellipse is significantly higher than the intensity of the reflection lying on the seventh ellipse, while in minerals with an illitic composition, the intensities of these reflections are almost equal.

The OSE features as well as the x-ray diffraction pictures permit the determination of differing degrees of structural order in the samples studied: from minerals with a three-dimensional ordered structure (the polytypical modification M), when the spatial hkl reflections, both with $k = 3n$ and with $k \neq 3n$, are fixed on the OSE, to structurally disordered minerals, when reflections with $k = 3n$ are present on the OSE but reflections with $k \neq 3n$ slip into the diffuse background (polytype 1Md). Here, the three-dimensional order of the mineral is not associated with the character of their mixed-layer nature.* In particular, it may be rather high for low-charge mica proper of different compositions and ages, which contain practically no swelling layers, and for mixed-layer formations of different ages, in which the number of these layers exceeds 20% (see Tables 3 and 4).

*Electronographic investigations proceed under conditions of a vacuum, which contributes to the removal of interlayer molecular water from the structure of the mineral and may lead to a higher three-dimensional order than in the natural mineral.

X-ray study of samples, having confirmed the differences mentioned above in the degree of three-dimensional order in the minerals and their mixed-layer nature, has also shown that the mode of their mica and smectite layer alternation is different. In particular, along with the unordered alternation of layers ($S = 0$), several hydromicas of different compositions have been encountered from Precambrian deposits with a tendency toward ordered interbedding of mica and smectite layers ($S = 2$ and 3).

Isomorphism in the octahedral positions of the minerals studied is also reflected on their IR spectra in the region of OH-group valence oscillations (Fig. 5).

Thus, dioctahedral 2:1 layered silicates, which form globules in the deposits of different ages studied, are represented by low-charge micas — glauconite, its Al variety, and illite, among which a continuous isomorphous series is observed. Each of these minerals in turn forms a structural series from mica to mixed-layer formation. A continuous isomorphism is also observed in hydromicas and mixed-layer minerals of different ages, which allows three continuous structurally isomorphous series to be distinguished for the entire assemblage of samples studied: glauconite → glauconite-smectite, Al-glauconite → Al-glauconite-smectite, and illite → illite-smectite. The representatives of each of these series differs in crystal chemical features and stratigraphic limitations. Glauconitic minerals are encountered in the Paleogene (Syria) as well as in the Lower Cambrian (Estonia and Siberia), minerals of the Al-glauconite series are widespread in the Upper Proterozoic (Siberia) and more rarely in the Lower Cambrian (Siberia), and illite and its structural varieties are characteristic only of the Upper Proterozoic (Siberia, the Urals), from the Lower Riphean to the Vendian, exclusively.

LITERATURE CITED

1. V. A. Drits and A. G. Kossovskaya, "Genetic types of dioctahedral micas: Report No. 1," *Litol. Polezn. Iskop.*, No. 5, 19-33 (1985).
2. B. B. Zvyagin, *Electronography and the Structural Crystallography of Clay Minerals* [in Russian], Nauka, Moscow (1964).
3. T. A. Ivanovskaya, "Transitional strata of the Cambrian and Precambrian in the Ulakhan-Sulugur section (middle course of the Aldan River)," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 1, 30-38 (1980).
4. T. A. Ivanovskaya and S. I. Tsipurskii, "Features of glauconite from Lower Cambrian deposits in the Ulakhan-Sulugur section," *Litol. Polezn. Iskop.*, No. 4, 79-86 (1982).
5. T. A. Ivanovskaya, M. M. Arkelyants, A. F. Veis, and S. I. Tsipurskii, "New data on the characteristics of Riphean deposits of the Mokui parameteric well (southeastern Yakutia)," *Litol. Polezn. Iskop.*, No. 6, 124-130 (1984).
6. T. A. Ivanovskaya, S. I. Tsipurskii, V. I. Cherkashin, and L. K. Takhontova, "Post-sedimentation transformations of glauconite in Riphean deposits of southeastern Yakutia," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 12, 108-118 (1985).
7. T. A. Ivanovskaya, "Mineralogy of dioctahedral micas in the glauconite group and sedimentary formations of different ages," *Candidate's Dissertation, Geological and Mineralogical Sciences, Moscow State Univ.* (1986).
8. A. G. Kossovskaya and V. A. Drits, "Problems in the crystal-chemical and genetic classification of mica minerals in sedimentary rocks," in: *Epigenesis and Its Mineral Indicators* [in Russian], Nauka, Moscow (1971), pp. 71-95.
9. I. V. Nikolaeva, *Minerals in the Glauconite Group in Sedimentary Formations* [in Russian], Nauka, Novosibirsk (1977).
10. I. V. Nikolaeva, V. A. Krasheninnikov, D. I. Golovin, and T. A. Ivanovskaya, "Possibilities for radiological dating based on glauconite in Paleogene deposits of the eastern Mediterranean," *Litol. Polezn. Iskop.*, No. 5, 76-88 (1985).
11. B. I. Omel'yanenko, I. M. Volovikova, V. A. Drits, et al., "The substance of the concept of 'sericite'," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 5, 69-87 (1982).
12. S. W. Bailey, G. W. Brindley, H. Kodama, and R. T. Martini, "Report of the Clay Minerals Society Nomenclature Committee for 1977 and 1978," in: *Clays and Clay Minerals*, 27, No. 3 (1979), pp. 238-239.
13. S. W. Bailey, G. W. Brindley, D. S. Fanning, et al., "Report of the Clay Minerals Society Nomenclature Committee for 1982 and 1983," in: *Clays and Clay Minerals*, 32, No. 3, (1984), p. 239.
14. H. A. Buckley, J. C. Bevan, K. M. Brown, et al., "Glauconite and celadonite: two separate mineral species," *Min. Mag.*, 42, No. 323, 373-382 (1978).

15. G. S. Odin, *The Glauconites: Constitution, Formation, Age* [in French], Doctoral Dissertation, Paris (1975).

COMPOSITION OF ELUVIAL PLACERS OF VIET NAM IN CONNECTION WITH ASPECTS OF LITHOGENESIS IN TROPICAL ZONES

L. V. Sporykhina, V. D. Belousov, and A. A. Petrochenkov

UDC 553.068.5(597.7)

Aspects of the formation of eluvial placers under conditions of long-term chemical weathering and formation of residuum were examined. The relationship of placers to the residuum is reflected in their morphology and size.

Eluvial placers that have a very close spatial connection with their bedrock sources are common in tin-bearing provinces of subequatorial zones, where they attain considerable size and are objects of commercial exploitation [1, 2]. Such placers have not been adequately studied in Viet Nam, and prospects for their discovery are not yet exhausted.

In Viet Nam the principle process of breakdown of bedrock, the first step in lithogenesis, is chemical weathering. The nature of this process is controlled by the modern hypsometric level for specific areas close to the seashore and by other base levels of denudation, such as the margins of persistent downwarps. The question of the age of the chemical-weathering residuum in Viet Nam is as yet unresolved. It was formed over a long period of time, at least the entire Cenozoic, and continues to form today. Products of chemical alteration of bedrock are widely encountered both in association with the modern surface of relief and in mineral components, and are represented by areal and linear residual weathering materials that occur in situ, by slightly displaced residuum, and by products of their redeposition.

In somewhat hilly, rolling denudational plains with elevations of 700-800 m, lateritic areas are found which vary in thickness, profile, and preservation depending on geomorphological setting and lithological substrate [3]. Thus, in the framework of accumulative intermontane basins in Cao Beng Province, on the gently rolling low mountain massif of Nu Phao, and in the framework to the northeast of the Tam Dao range, i.e., in the interior areas, an upper clay horizon is everywhere recognized, where the occurrence of primary rock can be determined on the basis of residual material weathered to quartz vein rubble, and also by different shades of individual clay layers. Excavation of this horizon indicates an apparent thickness of 3-4 m, rarely as much as 10 m. The rubbly horizon, as well as red color, can be traced downward through a gradational zone into eluvium. The total thickness of the rocks that have disintegrated and have been altered by chemical weathering ranges from a few to many tens of meters. For example, at Phuk Lin one of the drillholes penetrated 42 m of Triassic granite weathered to rubble; at Ban Chieng the depth of chemical weathering, represented by clayey material that contains rubble, exceeds 20 m; in placers of the Ngoi Lem valley, a drillhole 21 m deep failed to reach the base of the residuum; weathering of Upper Cretaceous tin-bearing granites at Pia Oak Junction reaches a thickness of 23 m, etc. Such large thicknesses of breakdown by chemical weathering are found in linear belts associated with tectonic faults of various ranks, and also linear contact zones along the margins of rock bodies of various compositions. On rising or stable coastal areas (Do Shon, Zu Long), as well as around structures with intensive neotectonic movements of different types (for example the Tam Dao horst and Red River graben), the upper clay horizon of the residuum is generally removed as a result of the action of denudational processes, and the present-day surface exposes rubbly residuum horizons or eluvium.

Above elevations of 700-800 m, residuum from chemical weathering is discontinuous and is found in areas of subdued topographic relief; it is dependent on lithology, or possibly it is preserved from an earlier weathering cycle. Moreover, patches of clayey residuum,

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sometimes quite thin, are found on somewhat flattened surfaces and in saddles; these apparently are to a considerable degree products of modern chemical weathering that have been formed on both residuum and bedrock.

Solution of carbonate rocks and karst formation, which are very characteristic of northern and central Viet Nam, are essentially a form of chemical weathering. The friable soil cover, considerably enriched in clayey and limy material, is known as *Terra Rossa*.

The result of intensive modern chemical alteration of rock and preservation of the older residuum from chemical weathering is a very high clay content in eluvial and slope deposits, and locally in alluvium. This in turn leads to the particular features of hillslope lithogenesis in Viet Nam. Here, even on steep slopes active talus, rubble, or block fields are absent. The fragmental material is submerged in a clayey mass which binds it rather securely. Mountain slopes of less than 20°, and especially slopes of the lower hills, are covered with a continuous, very stable mantle of clayey and rubbly material of more or less uniform thickness (3-6 m). Colluvium trains at the base of mountain slopes are usually lacking, while the low-relief foothill areas are commonly denudational forms developed on bedrock. Slopes with a positive-negative soil cover balance (except for very steep areas of colluvial drift) are virtually impossible to find. The soil cover is generally continuous on gentle slopes, but on steeper slopes it is discontinuous or even slumped; but the thickness varies little. Because of its high clay content and dense texture, permeability of the soil on the slopes is low, and intensive sheet erosion prevents a solid vegetational cover. In this connection, the presence of a high concentration of placer minerals directly on the surface or under the sod layer is probably due to surface erosion and local enrichment by removal of fines and solubles. Deposits of friable materials on slopes are emplaced in bulk by stream flow, including intermittent streams. This is explained by the high density of the drainage network and the large amount of precipitation, which together produce a large amount of this sort of drift. Slope processes themselves, creep, deflection, and deluvial erosion, accompanied by redistribution and gravitational sorting of the entire section, including commercial beds, take place much more weakly in Viet Nam than in arid, moderate, or subarctic climatic regions.

As a result, the formation of placers in normal slope deposits away from the source of supply is very difficult and is atypical here. In this regard, placers occurring on slopes in most cases are considered to be rather like slightly displaced eluvial deposits, marking the location of bedrock mineralization and occupying positions on the slope that are determined by the geomorphic position of the source material. Aspects of the distribution of unconsolidated material and productive deposits on slopes are graphically illustrated by the example of Bak Lung (Tam Dao placer-ore region).

The placer lies within a hilly, gently rolling basin with an absolute relief in the watershed of 100-105 m and local relief of 15 to 50 m. The slopes of the hills, hollows, and divides are covered by a continuous mantle of unconsolidated, essentially clayey material 4-6 m thick, following the topography (Fig. 1). The thickness of the unconsolidated material decreases somewhat (to 2-3 m) only in the bottoms of hollows, where the most active removal of fines and solubles takes place, leaving concentrations of heavy minerals. This fraction is distinguished by a higher concentration of placer cassiterite. In areas of placers, instances of increase in thickness (>10-14 m) of the unconsolidated material, not conforming to the modern topography and located on both divides and various slope areas, have been noted in mine workings that failed to reach bedrock. Judging by lithologic features and the distribution of the commercial components, in all cases of increased thickness we are dealing with the intersection of a linear residuum and a mineralized fracture zone, in which the higher cassiterite content in the rubbly unconsolidated material is followed by the mine drift.

The distribution of cassiterite in the Bak Lung placer is in pockets that are irregular in plane and section, corresponding to the distribution of the commercial component in the ore body. No leveling effect of downslope movement on the distribution of placer concentration was noted. Thus, the origin of the placer is essentially eluvial, associated with areal type chemical weathering residuum.

In placers of the Ban Chieng region (Fig. 2), the distribution picture for eluvial material is quite similar. The average thickness range is 6-8 m and rarely as much as 20 m or more, increasing over linear mineralized fracture zones and constant over various parts of the slope. This placer deposit is found in erosional-denudational low mountainous relief at an elevation of about 660 m and is limited geomorphically to erosional terraces with relative heights of

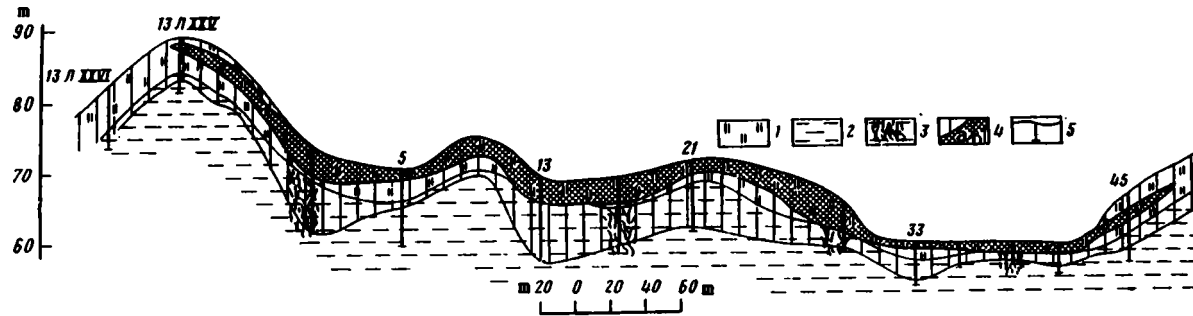


Fig. 1

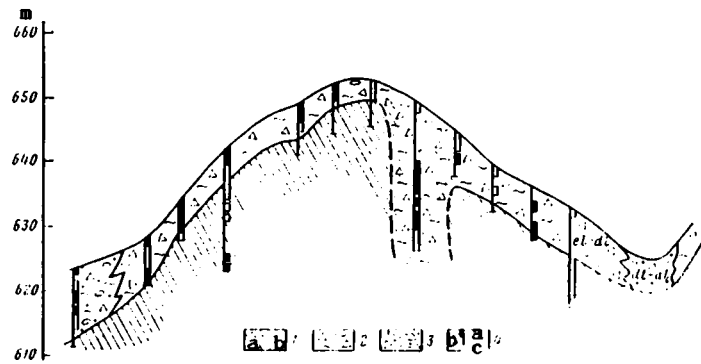


Fig. 2

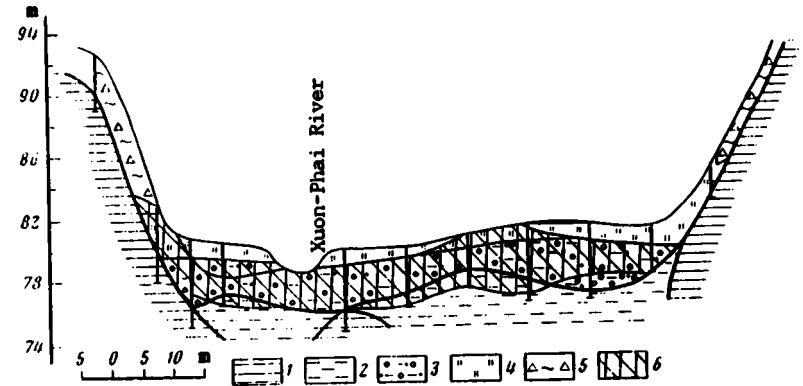


Fig. 3

Fig. 1. Part of the Bak Lung placer. 1) Eluvial gravel-rubble deposit; 2) eluvial shale; 3) presumed mineralized zone in shale; 4) placer concentrations (a, commercial; b, noncommercial); 5) numbered mine workings.

Fig. 2. Section across a placer deposit of the Ban Chieng region: 1) bedrock (a, shale; b, limestone); 2) eluvial material; 3) stream channel deposits; 4) cassiterite content in mine workings, kg/m^3 : a, >1 ; b, $0.1-1$; c, <0.1 .

Fig. 3. Section across Xuon Phai placers: 1) shale, 2) residuum over shale, 3) alluvium, 4) overlying loam, 5) slope material, 6) commercial placer bed.

80-120 m. Alluvium on the surfaces of these hills was preserved mainly in areas currently near valleys. Eluvial placers are partially buried beneath alluvium.

In contrast to Bak Lung, chemical weathering in the mineralized zone is much stronger here. Rubble, which is incorporated in clay masses, has practically entirely lost its strength and has been broken up and leached. This can be related to the generally higher dynamics of the low mountain relief in the Ban Chieng area compared to the denudational, low dynamics Bak Lung lowlands and to a more vigorous exposure to the effects of chemical weathering. Nor are the various aspects of hydrothermal activity in the mineralized zone in various ore placer deposits excluded. Distribution of cassiterite in placer bodies of the Ban Chieng region (as in Bak Lung placers as well) is irregular, which is associated with the nature of the mineralization of the bedrock source material. Moreover, the distribution of cassiterite in these areas is even more complex because of the fact that the area of ore occurrence is in the active erosion zone. The basal horizon of alluvium, preserved locally on the terrace slopes, is mixed with eluvium, somewhat displaced, and partially redeposited.

In addition to the eluvial placers, which occur at the surface and are associated with the present-day relief (Bak Lung) or are exposed as a result of removal of overlying deposits by erosion (Ban Chieng), small eluvial deposits buried beneath alluvium of the modern drainage network are also known in the tin-bearing regions of Viet Nam. For example, productive alluvium in the valley of the Xuon Phai River, with an average thickness of 5.5-6 m, is underlain by an essentially clayey tin-bearing residuum with an established thickness of more than 7 m (Fig. 3). In the Phuk Lin area, fine rubbly or clayey residuum, locally tin-bearing, also occurs in small hollows beneath younger surficial material of complex origin which is 2.5-8 m thick. The thickness of the weathered material, based on prospect pits, is more than 10 m. A zone of sharply increased thickness of friable rubbly-clayey tin-bearing material in a linear weathering zone has also been established for placer deposits in the Ngoi Lem valley. The width of the zone of cassiterite enrichment in eluvium is 20-60 m. The greatest concentration of cassiterite is not associated with the overlying tin-bearing alluvium, but with eluvial horizons. Tin-bearing residuum in valley bottoms is a source of introduction of cassiterite into younger alluvial placers, and ore can be extracted from both at the same time.

Thus, the following basic points can be made with respect to the features of eluvial placer formation in tin-bearing regions of Viet Nam.

1. Placers with a very high content of free cassiterite have formed in the chemical weathering residuum, regardless of the coarseness of the mineral or its relation to the bedrock.
2. Redistribution of the ore during slope movement redeposition is virtually absent due to the low dynamics of slope-cover processes.
3. There is a certain amount of enrichment in products of ore-bearing rock disintegration in place, as a result of removal of soluble compounds and mobile particles, with the formation of residual concentrations which are commonly at the surface.

In connection with these genetic features, this type of placer deposit in Viet Nam is characterized by: absence of a clear-cut correlation between such basic parameters of the placers as thickness of the commercial horizon and ore content: non-uniform and sometimes quite considerably thickness of the commercial horizon, commonly exceeding that in alluvial placers; irregular distribution of the ore component both vertically and horizontally in the placer deposits, determined by the distribution of cassiterite in bedrock ores and its breakdown by deep chemical weathering; and the much greater scale of these types of placer deposits compared to the Soviet Union.

LITERATURE CITED

1. S. F. Lugov and M. G. Rub (eds.), *Geology of Foreign Tin Deposits* [in Russian], Nedra, Moscow (1969).
2. S. I. Gurvich, *Patterns of Distribution of Rare-Metal and Tin Placers* [in Russian], Nedra, Moscow (1978).
3. V. M. Fridland, *Soil and Residuum of the Humid Tropics, in the Example of North Viet Nam* [in Russian], Nauka, Moscow (1964).

CARBON-BEARING ROCKS OF THE KHIRVINAVOLOK FORMATION,
NORTHERN KARELIA

V. T. Safronov and G. L. Goroshchenko

UDC 553.9(420.22)

The paper deals with the composition of sedimentary-metamorphic rocks of the Khirvinavolok Formation that caps the Lower Proterozoic section in the Kukas Lake area, northern Karelia. Two morphogenetic graphite deposit types have been found in these rocks. The analysis of the petrochemical parameters clearly indicates the low degree of maturity, the essentially terrigenous character and sandy-clayey composition of the sediments. The influence of tuff admixture on the composition of the primary sediments apparently was very limited.

Structurally, the subject area is located in the central area of the North Karelian synclinal zone, between the White Sea and Karelian Massifs and contains Lower Proterozoic supracrustal formations. The characteristics of the stratigraphy and lithology of the volcanic-sedimentary deposits in this zone have been earlier discussed [1, 5-9]. However, the lithology in several Karelide complexes is insufficiently known. The present work is the result of geology and the primary nature of metamorphic formations in the central Kukasozersk Syncline that is a feature, elongated in an east-west direction. It is traced for a distance of c.70 km and is 2-6 km wide. Along a significant distance the Kukasozersk structure is bounded by marginal faults along which the metamorphosed beds that form the syncline subsided in relation to the highly uplifted granite-gneiss margin zone. The rocks have been significantly dislocated and folded.

Two formations of different composition occur in the subject area: the Kukasozersk, a volcanic-sedimentary unit, and the Khirvinavoloksk Formation of carbonate-terrigenous [5, 6] composition. Rocks of the Kukasozersk Formation overlie the basement gneisses and are overlain by the Khirvinavoloksk Formation with its characteristic carbon-bearing components.

The terrigenous-volcanic Kukasozersk Formation contains two units; a lower, essentially volcanic (maximum 1600 m thick), and an upper, quartz schist-bearing (maximum 400 m thick) unit. The volcanic rocks consist of metamorphosed lava rocks, tuff breccias and tuffs that were converted into amphibolites, amphibole schists and amphibolites with amygdaloidal relic texture. In the upper unit, massive feldspathic quartzites are overlain by mica schists. The Kukasozersk Formation occurs along the south and north bands of Lake Kukas and forms the limbs of the Kukasozersk Syncline.

The central part of this syncline is composed of the Khirvinavolok Formation. Rock outcrops of the Khirvinavolok Formation occur on the Khirvinavolok Peninsula and in numerous Lake Kukas islands. High-carbon slates were studied on Petrov Island and numerous smaller islands east of Monastyrsk Island (Fig. 1). In addition practically all the studied sections with amphibolites and crystalline schists contained textural-structural features that indicate sedimentary origins; at the same time, the sections also contained amphibolites with textures that indicate igneous origin. They bear clear relicts of diabase structures of a quenched endocontact facies. In the hanging wall of these diabase bodies, a vesicular texture (amygdules) and preserved canals occur. These conduits conducted gases out of the hardening rocks. A typical example of the interaction between the Khirvinavolok sediments and the diabases that cut through them is shown in Fig. 2. The sketch is from an area where the most representative carbon-bearing schist-slate section occurs.

Those rocks were sampled for the study of the composition of metamorphosed schists and amphibolites in the Khirvinavolok Formation that indicated their primary sedimentary origins. A composite section of the primary sedimentary units of the formation, according to Krats [6] may be subdivided in the following fashion:

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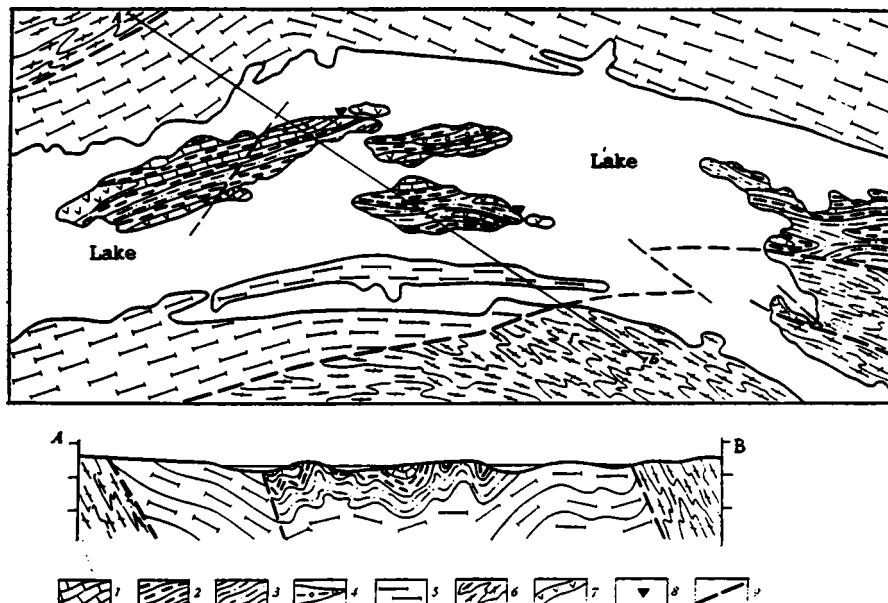


Fig. 1. Generalized geological map of the central areas of Lake Kukas. Compiled with data from Krats and Demidov. 1-3) Khirvinavolok Formation rocks: 1) interlayered carbonate-biotite-amphibolite schists, dolomites and limestones, high-carbon slates (units V and IV of the formation); 2) interlayered garnet-amphibole, garnet-staurolite (kyanite), amphibole-biotite-carbon-bearing schists (unit III); 3) amphiboles, garnet- and biotite-bearing amphibole schists, with rare quartzite layers (units I and II); 4) biotite-amphibole-quartz and feldspathic, carbonate-bearing schists, with rare plagioclase granite rubble and boulders; 5) undifferentiated Kukasozarsk Formation rocks; 6) undifferentiated, granitized; 7) amphibolized gabbro-diabase bodies; 8) high-carbon slates; 9) fault displacements.

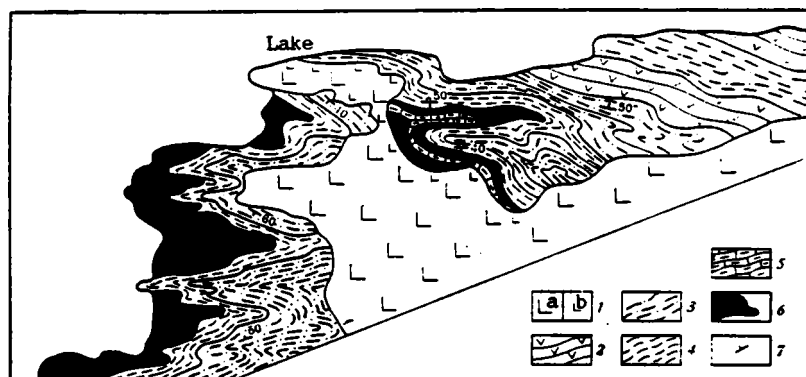


Fig. 2. Generalized geological map of carbon-bearing black slates in northern Petrov Island: 1) amphibolized diabases (a - coarse-crystalline; b - fine-crystalline); 2) amphibolites; 3) biotite-amphibolite schists; 4) garnet-biotite schists with graphite; 5) carbon-bearing black limestones; 6) carbon-bearing black slates; 7) foliation directions.

(I) Lower unit: composed of layered paraamphibolites, 200-250 m thick.

(II) This unit is composed of interlayered paraamphibolites and biotite-amphibolites and garnet-amphibole schists; 100-150 m thick.

(III) Interlayered carbonate rocks, amphibole-carbonates, staurolite-bearing schists and paraamphibolites. The thickness of the various rock subunits varies between 10-20 cm and reaches 1.5 m. The ratio of carbonate rocks increases upward in the section. Rhythmic

interlaying occurs. A flyschlike two-layer type is the most common: the carbonate layer is interlayered with various schists and amphibolite. The most complete rhythm at the base of the section is composed of garnet-biotite-amphibole schists - amphibolite-amphibolite with admixture of carbonate matter-calciphyre [3]. Thickness: 50-200 m.

(IV) Massive crystalline dolomites, often limestones. Rare layers of paraamphibolites, amphibole-biotite and garnet-staurolite schists. Thickness: 50-100 m.

(V) Carbon-bearing rocks top the section of this formation. Thickness: ~10m.

The rocks of the formation were nearly untouched by granitization; an indication of the isochemical character of the metamorphic process that reached conditions of the amphibolite facies [9]. Primary sedimentary layering, texture and structure were well preserved in the metamorphic schists. Layering was always well expressed; the beds and layers can be traced horizontally to certain distances. The carbon-bearing organic matter reaches 1% and occurs in almost all rocks of the formation. Its concentration increases upward in the section (Table 1).

In terms of organic carbon content, we have subdivided the rocks into the following categories: carbon-bearing (maximum organic carbon content: 1%), with higher carbon content (organic carbon content: 1-10%), and high-carbon rocks (organic carbon over 10%). Thermographic data indicate that the exothermal effect in the carbon-bearing matter starts at 620°C, with a maximum between 860-880°C. This suggests that the carbon-bearing matter in the rocks passed through the amphibolite metamorphic facies and structurally corresponds to graphite.

Our petrographic findings indicate that the organic matter accumulated in the rocks before metamorphism occurred, at the time when the primary sedimentary matter has accumulated. During deep metamorphic reorganization of the sediments the structural features of the organic matter have also changed and it was redistributed in the rocks. Figure 3a shows that the carbon (graphite) matter was redistributed as layers and patches, or evenly scattered throughout the entire rock body. The relict accumulation of carbon matter as microscopic laminae extend through amphibole and staurolite, rarely graphite porphyroblasts (Fig. 3b, c, d). In carbonate rocks it occurs both as layers and as patchy, nodular concentrates. Rocks of high carbon content are predominantly of massive, fine-grained texture and typically are of matte black color. They are composed of opaque carbon-bearing matter; graphite that carry minute quartz grains, minute mica flakes and larger amphibole grains. In high-carbon schists, graphite is more-or-less evenly distributed as minute flakes of 0.002-0.008-mm size. The graphite is a primary, syngenetic matter, formed from the organic matter in the rocks. There is also a more recent organic carbon concentrate that forms spherulitic aggregates, small veins and borders (Fig. 3e, f). Most frequently, the secondary morphogenetic graphite occurs in the intergranular space between large garnet and staurolite porphyroblasts, or as microlaminae. According to Sidorenko's classification [17] graphite in the Khirvinavolok Formation occurs as finely-dispersed and intergranular carbon matter in Precambrian sedimentary-metamorphic formations.

In the high-carbon Khirvinavolok Formation rocks ore minerals occur constantly. The most common are pyrrhotite, pyrite; less frequent, chalcopyrite and sphalerite. The sulfide content in the carbon-bearing rocks is 25-30%. Two morphogenetic sulfide types occur: fine pyrite and pyrrhotite grains, dispersed throughout the rock, and pyrrhotite and chalcopyrite grains, concentrated in thin veins and druses. Pyrite grains with graphite flakes are most common. Such combinations of graphite and ore minerals may indicate that ore minerals and organic matter occurred together in the source rock.

The primary sedimentary character of the metamorphic rocks that form the section of the Khirvinavolok Formation is clearly indicated by the textural and structural characteristics and the composition: the beds formed through the interlayering of essentially silicate, carbonate-silicate and carbonate rocks that contain organic matter with a wide concentration range. They display a great variety of chemical components (Table 1). However, the specifics of their sediment- and lithogenesis are clouded by the metamorphic reformation of the original rocks. For this reason, the lithologic study of metamorphic rocks of sedimentary origin requires a complex approach through geological-petrographic and petrochemical studies. Geochemical indicators often play a decisive role in this context [19]. Petrochemical indices, as Al_2O_3 , TiO_2 , etc. tend to be the most informative in distinguishing between correlated samples. Such indices often help petrographers to identify more exactly the genetic conditions of sedimentary matter in ancient basins; both of Phanerozoic and Precambrian age [7, 8, 20].

TABLE 1. Chemical Analysis Data of Khirvinavolok Formation Rocks (in %)

Com- ponents	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
SiO ₂	48.07	55.99	87.45	52.39	55.45	44.55	45.24	51.69	46.00	55.11	58.59	50.65	65.36	58.65	58.88	54.07	51.35	67.00	54.17	61.18	22.86	0.32
TiO ₂	1.01	1.43	0.25	1.40	0.60	1.28	1.09	0.49	0.81	1.23	0.74	2.73	0.72	1.68	1.53	0.68	1.23	0.83	1.71	1.00	0.16	0.17
Al ₂ O ₃	13.58	13.92	2.48	14.01	13.46	14.03	15.07	12.89	15.69	11.19	11.96	14.66	7.03	9.63	11.42	20.19	17.39	12.77	18.77	14.78	0.25	0.06
Fe ₂ O ₃	0.61	1.90	0.70	2.01	1.51	0.63	2.04	2.61	2.69	2.19	3.15	—	4.21	6.34	1.66	0.92	1.40	2.70	0.99	1.73	0.53	0.86
FeO	8.01	12.31	2.01	11.83	7.29	11.20	11.87	11.11	8.81	11.49	6.19	12.00	7.93	4.49	9.62	0.87	9.37	6.29	5.51	8.66	2.39	0.31
MnO	8.09	0.19	0.02	0.20	0.09	0.10	0.17	0.23	0.17	0.25	0.11	0.06	0.07	0.01	0.20	0.02	0.04	0.03	0.03	0.10	0.08	0.18
MgO	11.95	3.31	1.12	6.81	7.59	11.91	11.34	8.85	9.17	6.30	4.75	7.51	4.90	5.65	4.29	1.29	9.50	4.90	4.91	4.66	7.23	18.49
CaO	9.75	7.20	1.51	6.00	5.01	10.03	8.06	7.73	10.29	7.39	6.45	3.01	3.80	2.66	8.19	1.56	3.38	0.83	4.13	1.83	33.04	32.55
P ₂ O ₅	0.19	0.06	0.01	0.10	0.10	0.10	0.09	—	0.17	0.15	0.04	0.005	0.02	0.05	0.41	0.03	0.11	0.10	0.13	0.09	0.07	0.02
Na ₂ O	1.11	0.71	0.89	4.39	2.90	1.23	0.81	1.01	1.61	2.41	3.15	3.84	2.01	1.78	0.81	1.47	0.28	0.40	1.53	1.59	0.59	0.51
K ₂ O	0.49	0.61	0.13	0.10	1.93	0.70	1.28	0.40	0.47	0.11	0.61	0.52	0.22	0.25	0.23	6.10	1.58	0.67	3.93	1.59	0.11	0.07
H ₂ O ⁺	—	—	0.47	—	—	—	—	—	—	—	1.02	0.25	—	1.84	0.42	3.08	—	—	—	—	0.05	0.34
H ₂ O ⁻	0.02	—	0.08	—	—	0.22	0.10	—	—	—	0.06	0.46	0.40	0.57	0.06	0.46	0.22	0.11	0.23	0.07	0.15	0.15
CO ₂	0.97	0.30	—	—	1.71	1.30	0.50	—	2.98	—	—	0.34	0.16	0.45	—	0.30	0.61	0.13	1.66	—	21.85	45.20
C	—	—	2.90	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	8.20	1.44
Calcin. loss	3.07	1.86	—	0.70	2.73	2.00	2.23	0.66	1.60	1.60	2.69	3.55	2.61	5.69	2.00	8.80	—	2.78	3.63	1.90	1.93	—
Σ	99.92	99.79	100.02	99.94	100.37	99.28	99.89	100.33	100.46	99.42	99.51	99.58	99.50	99.74	99.72	99.85	99.24	100.39	99.66	99.98	99.47	100.77

Com- ponents	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44
SiO ₂	2.46	3.51	4.83	45.71	51.07	42.00	38.59	44.57	60.51	50.67	65.50	2.96	0.52	12.21	3.81	14.38	46.81	35.44	52.79	43.75	43.52	37.63
TiO ₂	—	—	0.08	1.13	1.33	1.45	1.77	1.19	0.85	1.07	0.71	0.08	0.17	0.17	0.03	0.23	0.68	0.77	0.77	0.67	0.68	0.52
Al ₂ O ₃	—	1.75	0.50	18.70	14.47	14.67	17.76	12.77	12.75	12.33	14.51	1.47	0.20	—	0.94	1.51	10.44	8.45	14.21	7.18	7.31	7.27
Fe ₂ O ₃	2.20	0.47	0.27	2.85	0.87	0.53	2.27	2.69	2.13	2.04	2.55	0.21	0.41	0.34	0.55	0.50	0.32	2.98	0.33	—	—	6.80
FeO	1.16	1.58	0.71	6.70	10.67	9.41	11.78	12.01	6.23	12.84	1.87	0.65	0.09	2.02	1.52	1.57	0.72	1.67	1.88	6.30	5.25	—
MnO	0.04	0.09	0.02	0.09	0.07	0.22	0.24	0.19	0.10	0.13	0.00	0.10	0.03	0.14	0.57	0.37	0.02	0.03	0.03	0.02	0.02	0.01
MgO	17.00	9.40	6.00	5.77	7.87	9.16	9.75	6.56	5.74	7.38	5.24	19.18	1.69	11.10	1.24	1.18	3.50	1.72	2.64	1.91	1.76	2.15
CaO	32.61	41.23	47.16	10.41	6.13	12.48	9.44	11.29	3.49	5.13	2.97	29.59	52.89	33.79	49.23	40.39	5.19	2.67	2.00	3.50	3.41	4.01
P ₂ O ₅	0.03	0.04	0.07	—	0.10	0.21	0.11	0.13	0.21	0.10	0.10	0.01	0.08	0.22	0.04	0.11	0.01	0.02	0.03	0.01	0.02	0.03
Na ₂ O	0.30	0.30	0.41	0.95	2.87	1.27	1.87	2.41	3.90	2.11	1.99	0.85	0.85	0.53	0.58	0.83	3.82	1.83	0.75	1.49	0.68	0.31
K ₂ O	0.16	0.15	0.00	2.33	0.11	0.33	0.31	0.29	2.00	3.37	2.23	0.38	0.22	0.07	0.07	0.09	0.81	1.33	4.45	1.93	1.05	0.61
H ₂ O ⁺	1.23	0.41	0.40	—	—	—	—	—	—	—	—	0.19	0.13	0.19	0.33	0.49	1.85	0.92	1.80	0.20	0.21	1.67
H ₂ O ⁻	0.06	0.04	0.10	0.24	—	—	0.10	0.10	0.21	0.13	0.06	0.15	0.22	0.19	0.02	0.26	0.20	0.18	0.43	0.45	0.35	0.38
CO ₂	42.80	40.83	39.95	0.80	—	—	—	—	0.96	1.25	0.91	42.79	42.75	37.65	39.36	32.68	0.65	0.80	0.75	—	—	—
C	0.64	0.79	—	—	—	—	—	—	—	—	—	1.80	—	0.30	2.32	5.25	25.20	49.80	17.10	33.10	33.00	32.00
Calcin. loss	—	—	—	3.82	4.57	2.04	5.88	4.61	0.99	2.20	1.15	—	—	—	—	—	—	—	—	2.43	5.34	—
Σ	101.42	100.53	100.59	99.50	100.13	99.77	99.82	99.71	100.36	100.71	99.85	100.41	100.25	99.57	100.28	99.84	100.22	99.73	99.96	100.51	99.69	98.73

Note. Unit I: 1) feldspathic paraamphibolite; 2) garnet-amphibolite schist; unit II: 3) black quartzite; 4) feldspathic paraamphibolite; unit III: 5) feldspathic paraamphibolite; 6-8) paraamphibolites with organic carbon; 9) feldspathic paraamphibolite; 10) garnet-bearing paraamphibolite with organic carbon; 11-15) garnet-biotite-quartz schists; 16) black sericite slate; 17-19) staurolite-biotite schists; 20) staurolite-biotite schist; 21) limestone with terrigenous admixture; 22-23) dolomites; 24) dolomite-bearing limestone; 25) limestone; unit IV: 26-30) paraamphibolites; 31) amphibolite-plagioclase schist; 32) garnet-amphibolite-plagioclase schist; 33) staurolite-biotite schist; 34) dolomite; 35) limestone; 36) dolomite; 37) limestone; 38) limestone with terrigenous admixture. Unit V: 39-44) high-C (graphitic) rocks. Samples 42-44 contain a total sulfur content of 1.27, 1.25, and 1.97%, correspondingly. Analyses performed at the Chemical Analytical Laboratory of the Geological Institute, Academy of Sciences of the USSR. Analyzed by I. L. Biryukova, G. F. Galkovskaya, and N. A. Kanakina.

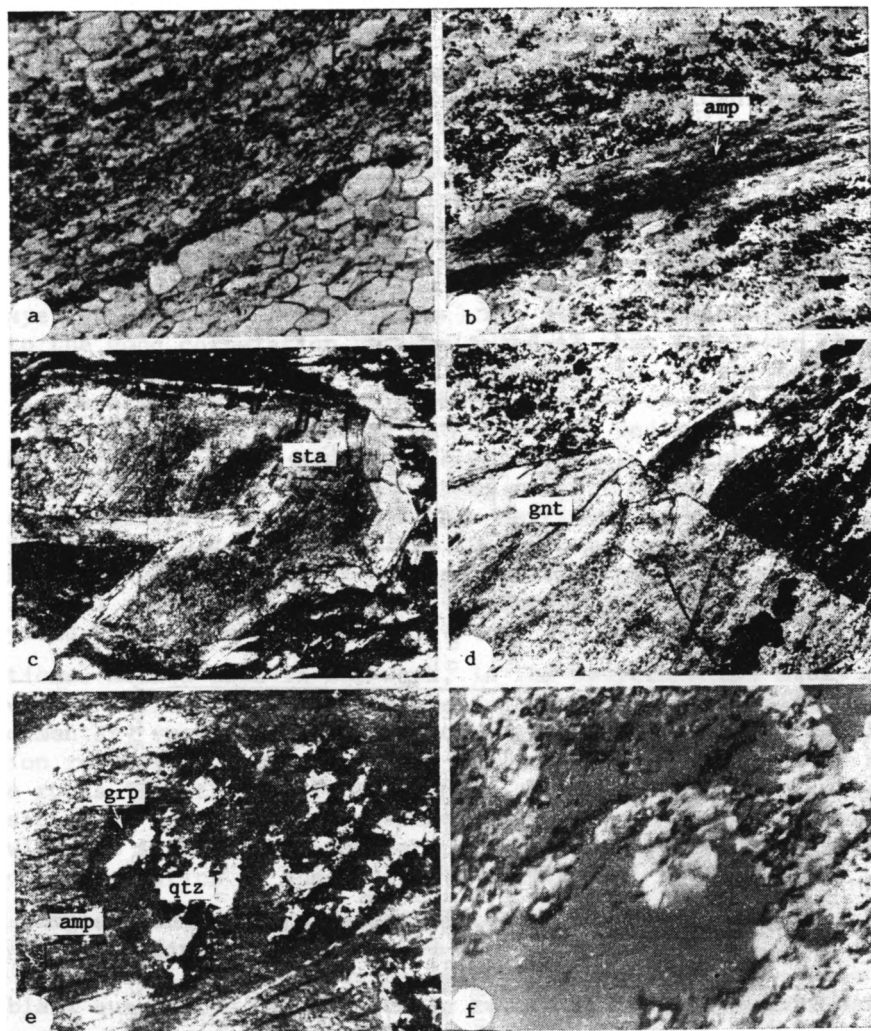


Fig. 3. Distribution pattern of carbon-bearing matters in rocks of the Khirvinavolok Formation. a) Layered carbon matter (black) in carbonate rock, thin section, parallel nicols, 180× magnification; b) thin layer of carbon matter (black) in amphibole quartz schist. (amp) amphibole porphyroblast, thin section, parallel polarizers, 180× magnification; c) relict carbon matter in staurolite (sta) porphyroblast, black: graphite concentrate in the basic matrix of garnet-staurolite-biotite-quartz schist; thin section, parallel polarizers, 180× magnification; d) relict carbon matter in garnet porphyroblast (gnt), black: graphite concentrate in the amphibolite background, thin section, parallel polarizers; 180× magnification; e) isolated graphite (grp) that enclosed quartz (qtz) grain, within poikiloblastic amphibole (amp). The amphibole contains dispersed carbon matter; thin section, parallel polarizers, 40× magnification; f) spherulitic graphite concentrate (light) in high-carbon slate, polished section, 750× magnification.

In identifying the primary composition of sedimentary rocks from which crystalline schists of the Khirvinavolok Formation, first we used petrochemical calculation methods, widely employed in the study of metamorphic formations [10, 12, 19]. The calculations were checked and confirmed through petrographic and geological findings. Those petrochemical calculations were used that, in combination, may indicate the type of the sedimentary source matter and the paleogeographic formation and accumulation conditions.

The association of the studied schist and sediment-derived amphibolite types with specific sedimentary rocks may be identified with the help of Neelov's diagnostic diagram [10] that involves terrigenous and terrigenous-carbonate deposits. The geochemical sedimentary

TABLE 2. Ratios of Petrogenic Elements of Khirvinavolok Formation Rocks

Unit number	Rock (number analyses)	$\frac{\text{Al}_2\text{O}_3}{\text{SiO}_2}$	$\frac{\text{TiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{Al}_2\text{O}_3}{\text{Na}_2\text{O}}$	$\frac{\text{Na}_2\text{O}+\text{K}_2\text{O}}{\text{Al}_2\text{O}_3}$	$\frac{\text{K}_2\text{O}}{\text{Na}_2\text{O}}$	$\frac{\text{CaO}+\text{MgO}}{\text{SiO}_2}$	$\frac{\text{K}_2\text{O}}{\text{Al}_2\text{O}_3}$	$\frac{\text{Fe}+\text{Mn}}{\text{Ti}}$	$\frac{\text{Al}_2\text{O}_3}{\text{TiO}_2}$
V	High-carbon type (7)	$\frac{0.16-0.27}{0.20}$	$\frac{0.05-0.157}{0.090}$	$\frac{2.37-18.95}{9.84}$	$\frac{0.23-0.48}{0.36}$	$\frac{0.21-5.93}{2.13}$	$\frac{0.09-0.19}{0.123}$	$\frac{0.08-0.31}{0.19}$	$\frac{1.98-12.30}{7.85}$	$\frac{10.72-18.45}{12.93}$
IV	Metamorphosed slates (3)	$\frac{0.21-0.25}{0.23}$	$\frac{0.05-0.08}{0.064}$	$\frac{3.25-7.43}{5.62}$	$\frac{0.29-0.47}{0.395}$	$\frac{0.51-1.67}{1.11}$	$\frac{0.12-0.25}{0.174}$	$\frac{0.15-0.27}{0.19}$	$\frac{7.90-20.13}{13.59}$	$\frac{12.38-20.90}{16.21}$
	Paraamphibolites	$\frac{0.28-0.46}{0.36}$	$\frac{0.06-0.10}{0.092}$	$\frac{4.98-19.87}{10.45}$	$\frac{0.10-0.21}{0.16}$	$\frac{0.03-2.51}{0.61}$	$\frac{0.27-0.51}{0.41}$	$\frac{0.006-0.13}{0.04}$	$\frac{10.39-14.31}{11.83}$	$\frac{9.75-16.10}{11.24}$
III	Metamorphic slates with with saturo'ite (4)	$\frac{0.19-0.35}{0.28}$	$\frac{0.016-0.03}{0.061}$	$\frac{9.50-67.31}{30.49}$	$\frac{0.08-0.29}{0.17}$	$\frac{1.03-6.00}{2.81}$	$\frac{0.085-0.25}{0.15}$	$\frac{0.05-0.21}{0.11}$	$\frac{4.88-14.25}{11.70}$	$\frac{10.75-16.09}{13.53}$
	Metamorphic schists with organic carbon (6)	$\frac{0.11-0.37}{0.22}$	$\frac{0.034-0.186}{0.115}$	$\frac{3.53-14.10}{7.40}$	$\frac{0.09-0.375}{0.27}$	$\frac{0.11-4.15}{0.84}$	$\frac{0.05-0.21}{0.156}$	$\frac{0.02-0.30}{0.08}$	$\frac{3.27-21.30}{10.64}$	$\frac{5.37-29.69}{12.37}$
	Paraamphibolites (6)	$\frac{0.20-0.34}{0.28}$	$\frac{0.036-0.112}{0.068}$	$\frac{4.48-18.75}{10.07}$	$\frac{0.11-0.36}{0.21}$	$\frac{0.04-1.63}{0.68}$	—	$\frac{0.009-0.15}{0.06}$	$\frac{11.65-37.07}{18.64}$	$\frac{8.90-27.72}{17.41}$
II	Paraamphibolites (1)	0.26	0.104	3.12	0.33	0.02	0.24	0.007	12.57	9.60
	Black quartzites	0.028	0.101	2.79	0.41	0.15	0.030	0.05	13.80	9.92
I	Paraamphibolites (1)	0.28	0.079	12.00	0.12	0.44	0.47	0.04	11.63	12.71
	Metamorphic slate	0.25	0.106	20.00	0.09	0.86	0.19	0.04	12.31	9.40

Note. The numerator shows range of values; the denominator, average values.

conditions are evaluated on the basis of indices of petrogenic elements. These petrochemical indices are the most informative in evaluating the paleogeographic conditions of sediment accumulation, composition of sediments and the impact of volcanic processes on sediment formation. The index values of rocks in all sections are given in Table 2.

The Si-index ($\text{Al}_2\text{O}_3/\text{SiO}_2$) is the measure of sediment maturity [21] and their composition and is among the most useful geochemical indices. The $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ and $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios similarly indicate the intensity of chemical weathering. The Ti-index ($\text{TiO}_2/\text{Al}_2\text{O}_3$) results from two, independent components: (a) primary Ti-content in the sedimentary source matter; (b) detrital sorting action [11]. The K-index ($\text{K}_2\text{O}/\text{Al}_2\text{O}_3$) is an important value, as its median values in clayey sediments (illite-chlorite) are always within a narrow range (0.1-0.3) [19]. This is due to the good correlation between K and Al that is closer than between Na and Al; as Al in the plagioclase represents only a small fraction of the total Al. Index values, lower than 0.1 characterize sediments in which chlorite or plagioclase predominates. High values most likely indicate feldspathic matter in the sediments. The total normative alkalinity index ($\text{Na}_2\text{O} + \text{K}_2\text{O}/\text{Al}_2\text{O}_3$) or Middleton coefficient is an indicator of Al-distribution in clay minerals and feldspars in the sedimentary rocks. Occasionally, this index helps in identifying volcanic matter in the rocks: within detrital and clayey terrigenous rocks the index usually remains between 0.2-0.4 [19]. The identification of volcanic matter in rocks of the Khirvinavolok Formation is a complex problem, as it can not be resolved through a search for direct lithological indicators of volcanic matter in metamorphosed rocks. Only petrochemical methods may yield the needed results [20].

An additional method used in our work, in the petrochemical study of metamorphosed sediments involves the recalculation of the chemical composition of metamorphic rocks for the normative sedimentary rock components, according to Rozen's procedure [12]. Table 3 indicates the calculation results of paraamphibolite chemical composition values and of various schists and carbonate rocks from the entire Khirvinavolok Formation interval, as figured for the normative composition of all possible sedimentary analogs. These data serve as supplementary data, along with the lithological-petrographic and geological findings, for establishing the comparative characteristics of the section's rock units.

Plotted composition values of amphibolites and garnet-amphibolite schists of units I and II occur in the sedimentary rock field of the diagnostic diagram; in the carbonate and iron-bearing clay field, while the garnet-amphibole schists plot in the polymict aleurolite field. The black quartzites of the section correspond to the quartz sandstone composition (Fig. 4).

In units I and II, the Si-index was 0.25-0.28, indicative of the low maturity level of sediments and of essentially clay composition. Values of the $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ and $\text{K}_2\text{O}/\text{Na}_2\text{O}$ indices indicate the extent of chemical weathering (values 3.1-20.0, respectively, 0.02-0.86) and are suggestive of a relatively low level of chemical weathering [4]. Low $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ (0.007-0.043) and $(\text{K}_2\text{O} + \text{Na}_2\text{O})/\text{Al}_2\text{O}_3$ (0.09-0.33) values indicate the relatively high Al-concentration in the rocks and that K and Al are mostly tied to clay minerals and not to feldspars. High (0.08-0.106) values of $\text{TiO}_2/\text{Al}_2\text{O}_3$ suggest that the source sediments of a given rock unit formed through the decomposition of basic rocks. It may reliably be suggested that volcanic matter was also enclosed in these sediments.

On the basis of their normative composition, the amphibolites and garnet-amphibole schists of units I and II correspond to carbonate-sandy clays and carbonate-clayey sandstones (Table 3) that contain significant amounts of quartz, plagioclase and chlorites. The normative composition of the chlorites of the source sediments has been determined by Rozen's method [13]. The calculations indicated that the Fe-index of the rocks ranges between 0.31-0.70. At this iron level, the chlorites of the source rocks appear to be of the prochlorite (ripidolite) group [2]. The significant ratio of normative plagioclase and Mg-Fe chlorites strongly suggest that volcanic tuff matter was part of the source rocks.

The investigated black quartzite of unit II appears to correspond to orthoquartzite [15] on the basis of its silica index (0.028). The carbonate index ($\text{CaO} + \text{MgO}/\text{SiO}_2$) was 0.03 and according to it, the studied quartzite unit originated from humid zone continental sands [14]. The high (0.01) $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratio confirms our conclusions that these quartzites had a terrigenous origin. In addition to quartz, the normative quartzite composition also includes minor amounts plagioclase, clay minerals, dolomite, and carbon (Table 3). Apparently, weathering crusts provided the source material of the quartzites. These crusts were widespread in the Baltic Shield area in pre-Yatulian times [1].

TABLE 3. Mineral Composition Norms of Metamorphic Rocks, Khirvinavolok Formation, in %

Mineral group	Minerals	Unit I		Unit II		Unit III				Unit IV			Unit V
		felspathic amphibolite (1)	garnet-amphibolite schists (1)	felspathic amphibolite	black quartzite (1)	amphibolite (6)	slates with organic carbon (6)	Al-schists (4)	carbonate rocks (3)	amphibolites (5)	schists (3) with amphibole, garnet, biotite and staurolite	carbonate rocks (2)	graphite-bearing rocks (6)
		1	2	3	4	5	6	7	8	9	10	11	12
Detrital	Quartz	22.44	28.15	16.32	79.19	17.83—28.12 22.70	5.21—45.38 29.35	23.71—44.01 32.64	0.0—2.94 0.98	4.70—21.28 14.19	18.95—39.33 27.23	0.60—8.90 4.75	16.28—30.69 23.35
	Plagioclase	9.32	—	38.07	8.15	6.83—27.15 14.60	0.0—34.39 18.66	0.0—15.42 7.58	2.52—2.83 2.66	4.07—25.41 14.41	18.19—36.22 24.46	4.70—7.26 5.98	0.0—34.01 12.92
	Orthoclase	—	—	—	—	—	0.0—11.88 1.98	—	0.0—1.12 0.37	—	0.0—7.31 3.98	0.0—0.55 0.27	0.0—8.07 2.20
	Total	33.76	28.15	54.39	87.34	37.30	49.99	40.22	4.01	28.60	55.67	11.00	38.47
	Clayey	Kaolinite	—	0.87	—	—	0.0—1.32 0.22	—	0.0—10.87 4.34	0.0—1.76 0.59	0.0—1.25 0.29	—	—
Illite		3.36	4.15	0.68	1.36	0.68—19.70 6.08	1.34—39.68 8.74	5.34—32.75 16.16	0.0—1.10 0.37	0.70—18.27 4.89	9.38—17.67 14.06	—	6.09—34.14 13.79
Montmorillonite		—	22.28	—	—	—	0.0—25.59 4.26	0.0—13.43 5.67	—	0.0—16.72 0.63	—	—	0.0—11.30 1.88
Chlorite		35.80	23.71	21.78	1.28	3.36—45.90 32.37	0.0—26.19 23.44	10.13—31.08 24.59	—	27.09—51.10 39.05	0.0—12.42 4.14	—	0.0—11.88 3.53
Sericite		—	—	—	—	—	0.0—2.54 0.65	—	—	—	0.0—8.48 5.46	—	0.0—1.42 0.26
Total		39.16	51.01	22.46	2.64	38.67	37.09	50.76	0.96	44.86	23.66	—	19.63

Iron bearing	Goethite			6,17	2,55	$\frac{0,0-7,97}{1,38}$	$\frac{0,0-8,09}{2,51}$	$\frac{0,0-2,87}{0,72}$	—	—	$\frac{1,38-16,11}{8,68}$	—	$\frac{0,0-4,17}{1,57}$
Carbonate-bearing	Calcite	3,40	5,43	—	—	$\frac{0,0-14,51}{4,63}$	$\frac{0,0-4,68}{1,42}$	$\frac{0,0-3,94}{1,70}$	$\frac{11,60-65,23}{41,03}$	$\frac{0,45-19,20}{12,48}$	—	$\frac{65,68-79,77}{72,72}$	$\frac{0,0-6,64}{1,90}$
	Ankerite	6,64	13,70	1,48	0,24	$\frac{0,0-11,52}{5,46}$	$\frac{0,0-12,95}{4,04}$	$\frac{1,05-4,43}{2,08}$	$\frac{2,90-9,58}{6,05}$	$\frac{0,0-8,08}{2,48}$	—	$\frac{5,99-6,02}{6,00}$	$\frac{0,0-2,98}{0,68}$
	Dolomite	15,63	—	13,64	4,10	$\frac{2,23-15,81}{9,82}$	$\frac{1,86-10,72}{5,96}$	$\frac{0,0-11,84}{2,96}$	$\frac{26,41-74,42}{47,49}$	$\frac{0,0-15,95}{4,24}$	$\frac{8,60-14,39}{10,55}$	$\frac{5,28-5,68}{5,48}$	$\frac{1,16-14,03}{6,11}$
	Total	25,67	19,13	15,12	4,34	19,91	11,42	7,46	94,57	19,20	10,55	84,20	8,69
	Carbon	—	—	—	2,84	$\frac{0,0-0,62}{0,10}$	$\frac{1,79-10,04}{4,30}$	—	$\frac{0,0-0,77}{0,47}$	—	—	$\frac{2,31-5,19}{3,75}$	$\frac{16,80-39,76}{29,49}$
Other minerals		1,41	1,71	1,86	0,27	$\frac{0,83-1,55}{1,28}$	$\frac{0,68-2,60}{1,51}$	$\frac{1,07-2,23}{1,56}$	—	$\frac{1,17-2,27}{1,72}$	$\frac{0,74-1,44}{1,13}$	$\frac{1,00-1,14}{1,07}$	$\frac{0,67-4,40}{2,10}$

Note. 1) carbonate-sand clayey and carbonate-clay sandstones; 2) carbonate-quartz; 3) carbonate-clayey sandstone; 4) essentially quartz sandstone; 5) carbonate-clayey sandstone and aleurolite; 6) clayey sandstone with carbonate; 7) sandy clay with carbonate; 8) sandy limestone and dolomite; 9) carbonate-sandy clay; 10) clayey carbonate-bearing sandstone; 11) limestone, with detrital admixture; 12) clayey, carbonate-bearing argillite. In brackets: number of full-chemical analyses of rocks. The numerator shows the range of components, the denominator, the mean values. All chemical analyses done at the Chemical Laboratory, Geological Institute, Academy of Sciences, USSR. The analyzed samples were collected by the present authors. Recalculation to normative composition according to Rozen method [12].

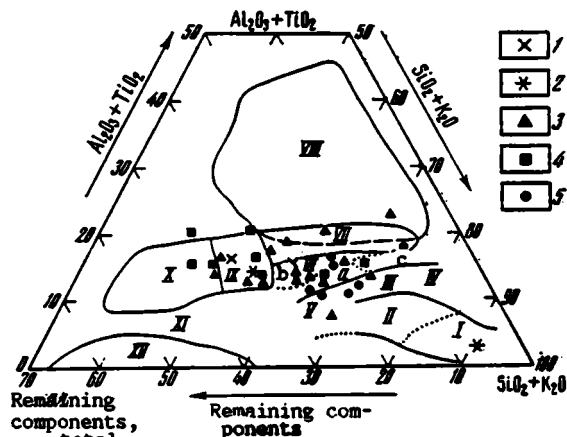


Fig. 4. Neelov's diagram [10] of the Khirvinavolok Formation rocks. Fields: I) quartz sandstones; II) oligomictic sandstones; III) polymict sandstones; IV) arkosic sandstones; V) limey, iron-bearing sandstones; VI) sediments, slightly differentiated chemically (a - gray-wackes; b - polymict aleurolites; c - sandstones with clayey cement); VII) chemically moderately differentiated clay; VIII) strongly differentiated clay; IX) carbonate and iron-bearing clay; X) marls; XI) siliceous marls, iron-bearing sandstones; XII) iron-bearing quartzites. Rock of the Khirvinavolok Formation: 1) amphibolites, garnet-amphibole schists of unit I; 2) amphibolites, quartzite, unit II; 3) amphibolites, staurolite and carbonate-bearing schists of unit III; 4) various schists and carbonate rock of unit IV; 4) high-carbon slates of unit V.

Within unit II, amphibolites, carbonate rocks, and crystalline schists are common. The schists include biotite, garnet, amphiboles, and staurolite. A significant portion of these rocks is composed of carbon-bearing organic matter. Most of the amphibolites of this unit plot in the carbonate and iron clay field of the diagnostic diagram, while the amphibole-bearing, carbon-bearing schists in the weakly differentiated sandy deposit field. The staurolite schists plotted in the field of slightly differentiated pelites (Fig. 4).

The value of the silica index in the staurolite schists ranged between 0.19-0.35, and between 0.20-0.34 in the amphibolites. This suggests the low maturity level of the source sediments. The silica index of essentially amphibole-bearing carbon-containing schists ranged between 0.11-0.37. Amphibolites and schists of unit III generally correspond to a wide range of terrigenous rocks on this basis; they range from aleurolites and sandstones to continental clays of humid zones [14]. Based on the Ti-index, with its average value of 0.061 in Al-rich schists; 0.115 in carbon-bearing schists, and 0.068 in amphibolites, it may be assumed that the parent rocks contained an abundance of weathering products, derived from the decomposition of basic volcanics, as well as significant amounts of tuff and sandy matter. This is confirmed also by recalculations to normative sediment compositions (Table 3). The $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ and $\text{K}_2\text{O}/\text{Na}_2\text{O}$ values generally were like for various rocks in unit III: the values were 30.5 and 2.81, respectively, in Al-schists, in carbon-bearing schists 7.40 and 0.84; in amphibolites 10.0 and 0.68. The data indicate the relatively low level of chemical weathering and slight differentiation of sediments in which significant amounts of chlorite and feldspars accumulated. Middleton's index, 0.4 in these rocks, suggests that the sedimentary parent matter was terrigenous in nature and the proportion of volcanic matter minor. The normative chlorite values of the sediment, assuming average iron content, were 0.41-0.50, suggesting the presence of prochlorite (ripidolite) [2].

The carbonate rocks of unit III consisted of dolomites, limestones, and mixed varieties. Individual carbonate beds contained major amounts of silicate minerals; quartz, feldspars, and mica. The recalculation of the carbonate rock content of unit III to normative mineral components in the sediments indicated that, on the average, they may have contained 4% detrital matter, less than 1% clay, while calcite and dolomite were present in approximately equal amounts (Table 3).

Amphibolite plots of schists of unit IV occur in the carbonate, Fe-bearing clay and marl field of the diagnostic diagram. Amphibole and staurolite schist varieties plotted in the

field of chemically slightly differentiated detrital rocks; such as graywackes and sandstones of clayey cement (Fig. 4).

The silica index of the amphibolites in this unit ranged between 0.28 and 0.46; corresponding to the index values of continental and lagoonal clays of the humid zone [14]. Average values of $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ and $\text{K}_2\text{O}/\text{Na}_2\text{O}$ (10.45 and 0.61, respectively) indicated the low degree of compositional differentiation of the source sediments. A series of average values ($\text{K}_2\text{O}/\text{Al}_2\text{O}_3 = 0.04$; $\text{Na}_2\text{O} + \text{K}_2\text{O}/\text{Al}_2\text{O}_3 = 0.16$) suggest that the amount of illites and feldspars in the source sediments apparently was minor and a large portion of Al occurred in the chlorites. These chlorites, according to normative composition, with a calculated amphibolite iron index of 0.48 correspond to the ripidolites. The biotite amphibole and garnet-staurolite schists of unit IV had a mean silica index value of 0.23 and low $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ and $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios (5.61 and 1.11, respectively). This shows a low level of parent sediment maturity and sandy-clayey composition. The index values of $\text{K}_2\text{O}/\text{Al}_2\text{O}_3 = 0.19$ and $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3 = 0.4$ suggest that feldspars and illites played an important role in the source sediments. In most of them, K was associated with illites and not with K-feldspars.

Recalculation of the composition of schists and amphibolites of unit IV to normative mineral composition (Table 3) indicated that these rocks correspond to carbonate-bearing clays and sandstones. Moreover, in normative feldspars, plagioclase predominates over K-feldspars.

Dolomites, limestones, and mixed rock varieties represent the carbonates in unit IV. Clean carbonate rocks with a CO_2 -content of over 40%, as well as carbonates with significant terrigenous admixtures (quartz and feldspars) occur. Carbon-bearing organic matter of 2-5% occur in the carbonate rocks; the organic origins of this matter may be indicated by the stromatolites in these rocks [16].

Unit V, which tops the Khirvinavolok Formation, is composed of graphite-bearing, matt-black rocks with 40% carbon content and usually less than 45% SiO_2 content. The high-carbon rocks of this formation plot in the chemically slightly differentiated rock field in the diagnostic diagram (Fig. 4): graywackes and polymict aleurolites with clay.

The silica index in unit V ranges between 0.16-0.27, indicative of the low maturity and the sandy-clayey nature of the sediments. Mean values of $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ and $\text{K}_2\text{O}/\text{Na}_2\text{O}$ (9.84 and 2.13, respectively) also suggest a low level of chemical weathering and the dominance of physical decomposition processes. Values of $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ (0.08-0.31) and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ (0.23-0.48) indicate the presence of feldspars and illite in the parent sediments.

The normative mineral composition of high-carbon slates corresponds to the carbonate-clay-sandy sediments in which the clay minerals consisted basically of illite, with minor amounts of chlorite; quartz and plagioclase in the detrital fraction, and dolomite represented the carbonates (Table 3).

This review of the petrochemical parameters of the Khirvinavolok Formation indicates that the sediments from which the paraamphibolites, the biotite amphibole the garnet amphibole and staurolite schists formed, essentially were of terrigenous origin and sandy-clayey composition. The carbonate rocks in the section contain a fraction of terrigenous admixtures. Analysis of the petrochemical parameters clearly indicates that the source matter had a low level of maturity and the source areas did not undergo intensive chemical weathering. Sedimentary differentiation of the matter was also minor, with the possible exception of quartzites of unit II. This is confirmed by the presence in the normative rock composition of such minerals as feldspars, illites, and chlorites.

The high carbonate index values to some extent may indicate the facies conditions of deposition. Its values in almost all rocks are higher than 0.1. This usually corresponds to marine conditions in geosynclinal zones where this parameter is 0.158 for sands and 0.182 for clays [14].

To a certain degree, the magnitude of the $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio may provide an estimate of the paleoclimatic conditions of deposition [4]. Rocks of the Khirvinavolok Formation are mostly characterized by values of this index, less than 20. Thus, the climate appears to have been essentially humid during the accumulation of carbon-bearing sediment sequence from which the Khirvinavolok Formation rocks of the Kukasozersk synclinal structure had developed. Such humid climate coincides with areas where life processes flourish.

The question of the ratio of volcanic tuff matter in the primary sediments remains an open one. It appears that certain petrochemical indicators suggest that most amphibolite, amphibole, staurolite and carbon-bearing schists of the Khirvinavolok Formation contain tuff matter. The rocks contain systematically high values of the Ti index and normative chlorites and plagioclase feldspars are abundant. However, in general, the normative alkalinity (G.2-0.4) remains within the range found, in regular terrigenous rock varieties [19]. Therefore, the impact of tuff matter on the composition of the primary sediment matter was very limited. A more exact estimate of the amount of tuff by direct petrographic studies in the metamorphic rocks of the Khirvinavolok Formation has not yet been possible to accomplish. Nevertheless, the presence of metadiabase layers in the section of the Formation clearly indicates that the chemical and mineral composition of the sediments had been influenced by postvolcanic gas and hydrothermal activity and this influence must be evaluated. The Fe-Mn index $[(Fe + Mn)/Ti]$ of Strakhov [18] was used to evaluate the possible exhalational origins of certain elements. In the studied rocks this index always remained within the range of 10-20, indicative of the absence of significant influence by exhalational matter during sediment formation of the Khirvinavolok Formation. Possible volcanic impact on the sedimentation may have only been possible through admixture of volcanic ash.

In conclusion, we call attention to certain paleogeographic configurations at the time of the primary sediment deposition in the Khirvinavolok Formation. One is certain; the studied sections occur in the axial zone of the synclinal structure and represent the interior part of the paleobasin that was close to the landmass. The constant proximity of the land during sediment accumulation is indicated by the terrigenous components in the rocks throughout the section. The Kukasozersk Syncline is an example of a small, shallow basin. Similar basins, associated with tectonically active rift-type zones were quite widespread during Karel'ian times in the Karelia-Kola Zone. The Pechenga and Imandra-Varzugsk structural zones [7, 8] have been the best studied ones. These contained sedimentary basins during Karel'ian times, filled under paleogeographic conditions that were identical to those in the Kukasozersk structure, by terrigenous-volcanic deposits that also contained carbon-rich sediments.

LITERATURE CITED

1. The Geology of Shungite-bearing Volcanogenic-Sedimentary Proterozoic Formations of Karelia [in Russian], (1982).
2. A. A. Godovikov, The Chlorite Group [in Russian], Nedra, Moscow (1975), pp. 278-289.
3. O. V. Gordachev, "Paraamphibolites and amphibole schists in Precambrian carbonate rocks," Problems of Precambrian Sedimentary Geology [in Russian], No. 6, Nauka, Moscow (1981), pp. 62-71.
4. Clay Minerals as Indicators of Lithogenetic Conditions [in Russian], Trudy Inst. Geol. Geofiz., Siberian Branch, Academy of Sciences of the USSR, No. 223, 9-37 (1976).
5. N. F. Demidov and K. O. Krats, "Stratigraphy and tectonics of the Kukasozersk-Tikshozersk Zone of the Karelides, northern Karelia," Trudy Inst. Geol. Karelian Division, Academy of Sciences, USSR, No. 20, 95-116 (1974).
6. K. O. Krats, Geology of the Karelides of Karelia [in Russian], Izd.-vo Akad. Nauk SSSR, Moscow-Leningrad (1963).
7. V. A. Melezhik, A. A. Predovskii, A. A. Basalae, and N. B. Bekasova, "Lithology and formation conditions of Proterozoic deposits of the marginal zone of the White Sea Megablock," Depositional Basins and Precambrian Volcanic Zones of the Kola Region. Apatites [in Russian], Kola Division, Academy of Sciences, USSR, (1983), pp. 5-32.
8. V. A. Melezhik and A. A. Predovskii, Geochemistry of Early Proterozoic Lithogenesis [in Russian], Nauka, Leningrad (1982).
9. N. I. Moskovchenko, "Composition and structure of rhythmic deposits in northern Karelia and conditions of their metamorphism," Problems of Precambrian Lithology [in Russian], Nauka, Leningrad (1971), pp. 69-84.
10. A. N. Neelov and G. V. Davydov, "Reconstruction of the original composition of sediment-derived metamorphic (para-) rocks, based on their chemical composition," Explanatory Text for Accompanying Geological Map of scale 1:50,000, Vol. 1, 397-400, Nedra, Leningrad (1974).
11. F. Pettijohn, P. Potter, and R. Siever, Sands and Sandstones [Russian translation], Mir, Moscow (1976).
12. O. V. Gordache, "Paraamphibolites and amphibole schists in Precambrian carbonate rocks," Problems of Precambrian Sedimentary Geology [in Russian], No. 6, Nauka, Moscow (1981), pp. 62-71.

13. O. M. Rozen, "Chlorites in sedimentary rocks," *Dokl. Akad. Nauk SSSR*, **228**, No. 3, 689-693 (1976).
14. A. B. Ronov, Yu. P. Girin, G. A. Kazakov, et al., "Sedimentary differentiation in platform and geosynclinal basins," *Geokhimiya*, No. 7, 763-776 (1966).
15. A. B. Ronov, M. S. Mikhailovskaya, and I. I. Solodnova, "Evolution of the chemical and mineralogical composition of sandy rocks," *Chemistry of the Earth Crust [in Russian]*, 201-253, Izd-vo Akad. Nauk SSSR, Moscow (1963).
16. Yu. I. Satsuk and V. V. Makarikhin, "Organic substances of the Middle Proterozoic rocks of Karelia, as indicators of paleogeographic conditions," *Problems of Precambrian Sedimentary Geology*, No. 4, Part 2, 180-184, Nedra, Moscow (1975).
17. Sv. A. Sidorenko and A. V. Sidorenko, "Organic matter in sedimentary-metamorphic Precambrian rocks," *Trudy GIN, Akad. Nauk SSSR*, No. 277 (1975).
18. N. M. Strakhov, *Geochemical Problems of Recent Oceanic Lithogenesis [in Russian]*, Nauka, Moscow (1976).
19. Ya. É. Yudovich, *Regional Geochemistry of Sedimentary Rocks [in Russian]*, Nauka, Leningrad (1981).
20. Ya. É. Yudovich, M. P. Ketris, A. V. Merts, and A. A. Belyaev, "Petrochemical diagnostics of volcanic rocks in the black shale deposits of Pai-Khoi," *Geokhimiya*, No. 6, 868-882 (1984).
21. F. J. Pettijohn, *Sedimentary Rocks*, 2nd ed., Harper and Row, New York (1957).

DEVELOPMENT CONDITIONS OF THE KOKZHOT SERIES IN KARATAU (KAZAKHSTAN)

Zh. S. Sargaskaev

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This paper describes the development of the carbonate-terrigenous Kokzhot series, which is subdivided into three suites: the sand-silt Kuyuk suite, the carbonate Botakara suite, and the Konurtobe sand suite. The study shows that the sediments were produced by autokinetic sedimentation in relatively deep-sea environments of submarine fans. The flysch nature of the carbonate-terrigenous formation is demonstrated.

In Southern Kazakhstan, within the Caledonides of the Kokchetav-North Tien Shan folded system, a peculiar carbonate-terrigenous formation is widespread: the Kokzhot series (1500-1600 m thick). The outcrops of the series are traced as a wide northwesterly strip between the structural-formational zones of the Lesser and Greater Karatau, separated from them by the Karoi overthrust and the Main Karatau fault on the northeast and southwest, respectively; the series extends beyond Kazakhstan and is seen in outcrops in the northern slopes of the Talass Alatau.

At the base of the Kokzhot structural-formational zone [19] a metamorphic complex of Lower Proterozoic is ascertained. With a large interruption it is overlain by the Kokzhot series; its rocks are strongly dislocated, with widespread isoclinal folds and cleavages. Along with linearly stretching large folds of the first order, smaller folds are common, up to microfolding. The degree of dislocation increases near tectonic faults. The rocks there become quartz-sericitic, quartz-chlorite-moscovitic blastopsammitic and blastosiltstone schists. According to faunistic finds [10], the age of the Kokzhot series has been determined as Vendian-Middle Ordovician. The series is divided into suites (bottom to top) [1]: sand-silt Kuyuk suite; carbonate Botakara suite; and sand Konurtobe suite.

In the northwestern part of the zone the Kokzhot series is overlain, also disconformably, by molasse-like formation of the Middle Devonian Tyul'kubash suite.

Institute of Geological Science, Kazakh Academy of Sciences, Alma-Ata. Translated from *Litologiya i Poleznye Iskopaemye*, No. 1, pp. 70-81, January-February, 1988. Original article submitted March 3, 1986.

TABLE 1. Tuffogritstone Rock Association

Feature	Small-grained gritstone, coarse- to medium-grained sandstone	Small-grained sandstone, siltstone, argillite
Rock color	Grayish-green	Greenish-gray, gray, brown on a weathered surface, sometimes black
Sorting	Poor. Inequigranular. For small-grained gritstone and coarse-grained sandstone maximum size 3.3 mm, minimal size small-grained silty, medium size 0.8-1.3 mm. For medium-grained sandstone the maximum grain size is 2.2-1.0 mm; minimal grain size as in microgranular siltstone; average size 0.6 mm	Poor. Inequigranular. Maximum grain size range 0.9-1.1 mm; average size 0.09-0.2 mm; minimal size as in small-grained silt. Elongate fragments of clay schists ranging in size from 2.5 to 0.6-0.7 mm are frequent.
Structure	Direct gradational, sometimes inverted stratification. Various bed base signs are widespread: hieroglyphs. Clayey intraclasts and distinct erosional lower contacts are typical.	Horizontal and oblique unidirectional stratification
Reworking of material	Semiangular, less often rounded. Single sharply angular quartz fragments - tephrogenic material - are characteristic.	Semiangular, angular, less often rounded. Sharp and angular fragments (sometimes with melted quartz edges) of rocks with a microfelsite groundmass texture are found: tephrogenic material.
Composition of fragments: Edaphogenic clastics of the first kind	Basaltoids, andesites, diabases, hyaloclastites associated with them, silicic rocks, rounded fragments of marble, single grains of altered amphibole, monoclinic pyroxene; accessory minerals: chromespinelide, titanomagnetite, and ore minerals.	Single grains of basic and neutral effusives; marble fragments.
Edaphogenic clastics of the second kind	Argillite, siltstone, oligomictic small-grained sandstone.	Argillite
Sialic clastics	Quartz, often cataclased small-grained granite, effusives and tuffs of an acid composition, quartzmica schist, quartzite, oligomictic small-grained sandstone, microgranophyres, potash feldspar, altered feldspar; accessory: monazite, etc.	Quartz, quartzite, acid effusives and tuffs, small-grained granite, albitized potash feldspar, and feldspar. Single monazite grains.

TABLE 1 (continued)

Feature	Small-grained gritstone, coarse- to medium-grained sandstone	Small-grained sandstone, siltstone, argillite
Cement:		
a) composition	Silicic-sericite-chloritic, micaceous-chloritic, sometimes micaceous-chlorite-carbonate.	Chlorite-micaceous with leucoxene and rutile needles; carbonate cement
b) cementation type	Contact, less often pore filling. In medium-grained varieties (pore fillings, less often basal). Uniform distribution of fragments.	Basal, uniformly distributed, locally in clusters.
c) amount of cement	Sparse cement (5-7%)	Abundant, 15%
Complex of associated rocks	Green argillite, small-grained sandstone	Sandstone
Genetic sediment type	Sediments of grain flows or immature turbidites	Interturbidite sediments genetically associated with calm (pelagic) sedimentation reworked by contour or bottom currents
Tuffs		
Rock color:	Turquoise	
Grain size, mm:		
a) predominant	Maximum dimensions 0.4-0.8 mm; minimal dimensions as in small-grained silt. Average dimensions from 0.08-0.09 to small-grained silt.	
b) admixture	Fragments of clay schists 1.9 mm long and 0.3 mm across	
Sorting	Poor	
Texture	Small porphyritic	
Grain composition:		
a) predominant	Albitized potash feldspar, quartz	
b) admixture	Clayey schist, silt, quartzite, fragments of chloritized volcanic glass	
Grain shape:	Tephrogenic matter: angular, fragmented, fork-shaped. Terrigenous clastics: rounded	
Groundmass:		
a) composition	Abundant quartz, albite, silica, and micas (muscovite and biotite) and chlorite with leucoxene	
b) texture	Porphyritic. The groundmass is fine- and small-grained	
c) amount and type	Uniformly distributed, abundant, cryptogranular, ash 90 to 95%	
Structure	Laminated. Direct granulometric differentiation of matter is typical. At the bottom of the layers the tuff is enriched in crystalloclasts, less often lithoclasts; at the tops the rock becomes cryptogranular ash tuff	
Associated rocks	Medium- to small-grained sandstone, siltstone, and argillite	
Genetic type	Telepyroclastic sediments	

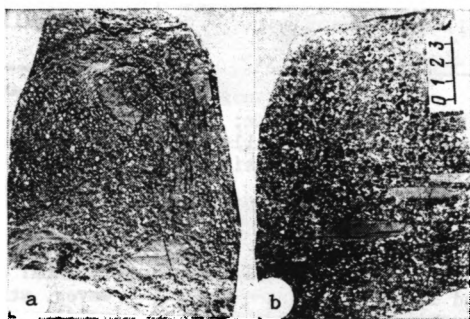


Fig. 1

Fig. 1. Argillite intraclasts in a sand matrix: (a) horizontal cross section (reduced 6.0×); (b) vertical cross section.

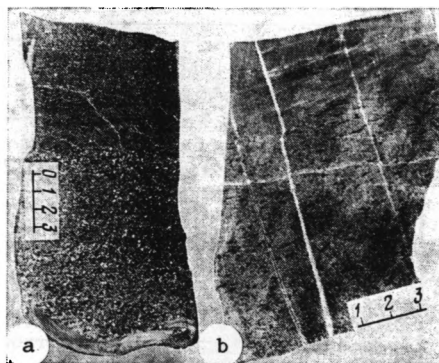


Fig. 2

Fig. 2. Genetic types (sediments of streams): (a) grain streams; (b) turbidite streams.

A lithologic study of the carbonate-terrigenous formation has determined features of stratification, structure, texture, and mineral composition indicating that the sediments belong to flysch. Flysch formations are the subject of extensive studies [4-7, 11-14, 18, 21, etc.]. The diagnostic features of the genetic types of sediments isolated in this study have been described in detail by Frolov [20].

The Kuyuk suite is most developed within the Kokzhot block and does not vary laterally along the course. It consists of gray-green argillite, siltstone, small- and medium-grained, less often coarse-grained sandstone, gritstone, tuffosandstone, and tuff. Pyrite crystals are typical. Two rock associations are distinguished: tuffogritstone and sand-silt.

The tuffogritstone association (Table 1) tends to occur at the bottom portions of the profiles and is represented by small gravel coarse-grained psammitic varieties (bed thickness from 0.5 to 2-3 m) with rare interlayers of small-grained sandstone, siltstone, and argillite. Single small (several centimeters) pebbles are found which consist of small-grained polymictic sandstone similar in composition to the enclosing rocks.

The clastics of the detrital rocks are polymictic with a large amount of lithic fragments, sometimes with an admixture of tephrogenic material. In the lower third of the section of a single horizon of vitroclastic acid tuffs up to 10 m thick is observed.

The association is characterized by a distinct sometimes blurred rhythmic stratification; less often, massive structures are found in small-grained sandstone beds. In layered varieties a direct gradational distribution of material typical for turbidite structures is observed, as described by Bouma [26]. There is a gradual transition from coarse-grained sandstone at the base of the beds to medium-grained at the roof. Microstratified argillites are often present in the bed roofs. Inversional roughening of material from silt to psammite sizes is sometimes observed at the tops of the multilayers. Finely stratified layers (from 1.5 cm thick) of argillites and siltstones at the base of such beds gradually are succeeded toward the roof by medium-grained sandstone with minor admixtures of clay cement (a few percentage points). The formation mechanisms of these structures have been described by Walker [28].

The lower contacts of the graduated beds are always sharp and may be horizontal, wavy, or erosional. The upper contacts are either sharp or gradual. At the base, and less often within the beds, ellipsoidal interclasts of clay schists are present, intruded into the sand matrix apparently during the "plowing" [27] of the silty bed by turbulent streams. The fragments vary in size from a few centimeters to 12 cm and more. These peculiar interformational conglomerates are typical for sediments with an alternation of sand and clay (Fig. 1a, b).

The structural and textural features such as the substantial thickness of cyclites (up to 2.5 m), the coarseness of the clastic material, the small amount of binding matrix (cement 5-7%), the erosional contacts, the presence of intraclasts, the gradational and locally inverted sorting of clastic material, and the base signs all indicate that these sediments are deposits of grain flows or immature turbidites formed in the proximal zones of deep-sea submarine fans (Fig. 2a).

TABLE 2. Sand-Silt Rock Association

Feature	Coarse- to medium-grained sandstone	Small-grained sandstone	Silt, argillite
Rock color	Greenish-gray	Greenish-gray,	sometimes black
Sorting	Poor. Inequigranular. Maximum size 0.9-1.2 mm; minimum size as in small-grained silt; average size 0.6-0.8 mm; most frequent grain sizes from 0.15 to 0.20 mm	Poor. Maximum size 1.0 mm; minimum size as in small-grained silt; average size 0.1-0.2 mm	Medium
Structure	Direct gradational. Surface structures-hieroglyphs-are frequent. Sculptures of stream jets, burrows, and intrusion signs are observed. At the base of the graduated series thin interlayers (0.4 cm) of medium-grained sand material ("drag carpet") are frequent		Horizontal and oblique wavey, stream-type unidirectional lamination. Upper and lower contacts are contrastive
Reworking of material	Terrigenous clastics are semi-rounded, sometimes angular. Tephrogenic material: angular, fragmented, fork-shaped, less often with melted edges	Terrigenous clastics: semirounded, less often rounded. Tephrogenic material: angular, broken	
Fragment composition: Edaphogenic clastics of the first kind	Basic and neutral effusives, silicic rocks, rounded marble fragments, individual grains of amphibole and monoclinic pyroxene	Individual fragments of basic and neutral effusives, marble, and silicic rocks	
Edaphogenic clastics of the second kind	Argillite and siltstone	Siltstone and argillite	
Sialic clastics	Quartz, often cataclased quartzite, acid effusives, and tuff oligomictic small-grained sandstone, quartz-mica schist and feldspar	Quartz, quartzite, acid effusives and tuffs, feldspar. Tephrogenic material: quartz.	
Cement:			
a) composition	Chlorite-sericitic	Chlorite-sericitic	
b) cementation type	Pore filling, locally contact-type, basal cement	Basal, less often pore filling	
c) amount of cement	10%	15%	10%
Complex of associated rocks	Siltstone, argillite	Argillite	Siltstone
Genetic type of sediment	Sediments of turbidite flows formed in distal portions of deep-sea fans as opposed to the rocks of the tuff-gritstone association		Interturbidite. Calm (pelagic) sedimentation products, contourites

The beds of coarse-grained rocks are divided by thin (up to 10 cm) multilayers consisting of thinly alternating siltstones and argillites with a horizontal or oblique unidirectional stratification. We identify these layers as interturbidite units associated genetically with sediments of calm (pelagic) sedimentation reworked by contour or bottom flows.

The horizon of vitroclastic and vitrocryсталloclastic tuffs (see Table 1) of an acid composition is traced distinctly along the course for many kilometers (it is 10 m thick). The lower contacts of the bed are even or gently wavey; the upper contacts are slightly erosional due to partial washout by later suspension streams of terrigenous matter. A granulometric differentiation is typical for the tuffs. At the lower parts of the bed the tuff is massive and "enriched" in crystalloclasts of quartz, albitized potash, feldspar, and rare lithoclasts. The grains are angular, fork-shaped, fragmented, with maximum size of 0.4-0.8 mm. Up the section the tuff becomes ash tuff; it is a cryptogranular rock with relicts of fork texture. Horizontal thin layers of ash material (2 cm and less) interstratify with clay layers (a few millimeters). The upper and lower discontinuity surfaces of the layers are gradual and even. The tuff horizon was apparently formed in connection with the activity

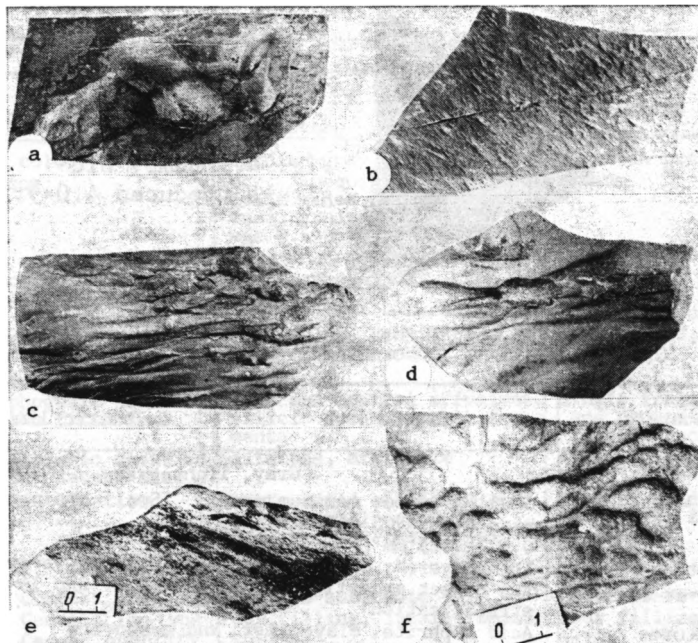


Fig. 3. Hieroglyphs (mechanoglyphs): (a) chaotic sculptures of intrusion at the base of the sand bed overlying a clay bed (reduced 5.0 $\times$); (b) imprints on the bottom: "drag signs" (reduced 4.0 $\times$); (c) signs: sculptures of erosion furrows; lower surface of medium-grained sandstone occurring on argillite (reduced 45.5 $\times$); (d) signs: sculptures of stream jets (reduced 4.0 $\times$); (e) signs of washout jets of sandstone; (f) signs of intrusion appearing as bumpy wrinkled surface with unclear linear orientation of elements; occur on the lower surface of sandstones underlain by clayey argillite crumpled to small folds.

of distant highly explosive volcanoes from which ash was carried by air and precipitated through the water.

Sand-silt rock associations (Table 2) are most developed at the tops of the strata. They consist of gray-green, gray, small-grained, less often medium- to coarse-grained sandstone, siltstone, and foliated argillites. The clastic matter of detrital rocks is polymictic with substantial amounts of tephrogenic material.

The association is characterized by direct gradational sorting of clastics with grain size varying up the bed from psammitic to coarse-grained silt varieties (see Fig. 2b). At the base of the graduated series, thin (0.4 cm) interlayers of medium-grained material are often seen ("dredging carpet"). The sand element of the cyclite is predominant; it is 35-40 cm thick, sometimes 1 m; the thickness of fine-grained elements is not greater than 10-15 cm. Cyclites of several types are typical: medium- and small-grained sandstone-siltstone, siltstone-argillite, small-grained sandstone-siltstone-argillite. A similarity with the sequence of the turbidite series described by Bouma is discernible. The following elements of Bouma's model are identified: A, AB, ABE, AE, less often ABCE and ABCDE. The bottom contacts of sandstone beds are sharp; they are even, sometimes fibrous. Slump structures and foot signs are often observed; the sizes of the signs are proportional to granularity. The upper contacts are even, sometimes gradual. Structures in the form of subparallel bars are clearly seen in some locations; they were formed by partial erosion of sandstone substrate by bottom currents.

All terrigenous rocks of the association are similar in sorting and processing of fragments and content of binding cement. Material is poorly sorted. The fragments are semi-rounded, sometimes angular. The composition is variegated. A large proportion (10-15%) of the clay matrix of a chlorite-sericite composition indicates that these clastic rocks belong to the graywacke group according to Pettijohn's classification [17].

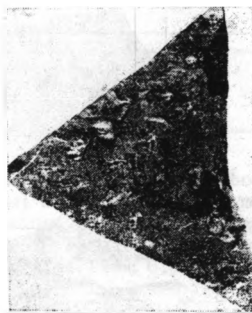


Fig. 4. Bumpy bioglyphs (reduced 4.0×).

TABLE 3. Carbonate Rock Association

Feature	Limestone	Dolomitic limestone
Rock color	Gray, light-gray	
Texture	Small-grained; maximum grain size 0.03-0.05 mm; average 0.02-0.025 mm	Small-grained
Stratification pattern	Thin-layered; characteristic direct gradational stratification	Oblique wavey; sharp upper and lower contacts
Main admixtures	Acid tephrite, claymatter, and muscovite	
Paragenesis	Alternation of fine stratified limestone and clayey green sheet argillites	
Genetic sedimentary type	Carbonate turbidites	Sediment of contour currents

Surface structures - hieroglyphs (mechanoglyphs) - are frequent in terrigenous formations [3, 9, 22], which are the typical traits of sediments deposited by autokinetic flows. Sculptures of jets of currents and furrows of various morphology have been observed as protruding linear elements on the bottom surface of sandstone beds. Intrusion elements are less frequent; they are formed by the impression of coarser matter into clay; they are also asymmetric signs of small-scale flow ripples seen as parallel ribs (Fig. 3a-f).

An investigation of the clastics in detrital rocks and the textural and structural features (poor processing and reworking, large amount of cement, and elements of Bouma's [26] turbidite model, foot signs, and stratification pattern) indicate that these formations are sediments deposited by turbidite flows in distal parts of deep-sea fans, as opposed to the rocks of the tuffogritstone association according to Walker's model [28].

Besides the gradational-stratified members the association includes interlayers of siltstone and argillite with sharp upper and lower contacts. These are multilayers 8-25 cm thick consisting to groups of thin layers with horizontal and oblique-wavey unidirectional flow-type stratification [2]. Obliquely layered packets are apparently linked genetically with bottom contour flows, while massive layers with horizontal stratification were formed in a calm (pelagic) sedimentation environment. Alternating intervals with oblique and horizontal stratification show that unidirectional flows were sporadic and interchanged with calm sedimentation regimes.

Hieroglyphs of a biogenic origin, seen as small protrusions on the surface of silt layers, occur less frequently (Fig. 4).

Studies of the mineral composition of rocks of the suite as a whole determined that they are formed of materials that arrived from different sources: a) from land (sialic clastics) and b) due to erosion, denudation, and redeposition of the products of decay of bedrocks of the seafloor and weakly lithified sediments (edaphogenic clastics) [8, 15, 16].

Sialic clastics consist of fragments of various granulometric types, including quartz, altered feldspar and acid tuff, oligomictic small-grained sandstone, quartzite, quartz-micaeous schist, small-grained granite, various acid effusives, albitized potash feldspar, mica, single microgranophyre grains and accessory monazite and glauconite. The quartz grains are cataclased.

Edaphogenic clastics of the first kind were formed as a result of erosion of protrusions and ledges of the seafloor formed by older Proterozoic enclosing rocks. It includes basal-

TABLE 4. Sandstone Rock Association

Feature	Coarse- to small-grained sandstone	Siltstone argillite
Rock color	Greenish-gray	Greenish-gray
Sorting	Poor. Inequigranular. Grain sizes from 1.5 mm to small-grained silt. Average 0.6-0.8 and 0.15-0.20 mm	Medium
Structure	Direct gradational. Bed base signs	Horizontal, oblique undirectional. Sharp upper and lower contacts
Reworking of material	Semiangular, semirounded, less often rounded	Semirounded, rounded
Fragments:		
Edaphogenic clastics of the first kind	Basic and neutral effusives, silicic rocks, marble fragments	Single fragments of basic and neutral effusives, silicic rocks
Edaphogenic clastics of the second kind	Siltstone, argillite	Siltstone, argillite
Sialic clastics	Quartz, acid effusives and tuffs, small-grained granite, quartzite, feldspar	Quartz, acid effusives and tuff, feldspar
Cement:		
a) Composition	Chlorite-sericitic	Chlorite-sericitic
b) Cementation type	Poor filling, locally basal	Poor filling, locally basal
c) Cement quantity	10-15%	5-10%
Complex of associated rocks	Siltstone, argillite	Sandstone
Genetic sedimentary type	Massive sandy turbidite	Interturbidite. Calm (pelagic) sedimentation products, contourites

toids, andesites, diabases, silicic rocks, and hyaloclastites. Rounded marble fragments, single titanomagnetite grains, chrome spinel, monomineral strongly altered monoclinic pyroxene, and amphibole are also found. The largest quantity (10-15%) of these clastics is observed only in coarse-grained sediments of the tuffogritstone association; in others, only single fragments are found.

Edaphogenic clastics of the second kind produced by autokinetic flows eroding semilithified and lithified earlier-deposited material are quite common in clastic rocks of the suite (mean contents of 10-15%, maximum contents 20% in the tuffogritstone association). Breakaway elements and rounded fragments of lithified fine-grained sediments were redeposited and brought into almost contemporaneous neomorphous rocks. The structures formed in the process were typical for grain flows. The clastic matter consists of argillites and siltstones.

All rocks of the suite have fragments of a similar mineral composition. The quantitative proportions of clastic materials of various origins, however, vary depending on the granulometry and genetic type of the sediment. In the top sand-silt association the coarse-grained sandstones are more polymictic (the maximum content of the edaphogenic clastics of the first kind) and the proportion of tephrogenic material is higher. The tephrogenic material consists of quartz and rock fragments with a microfelsite texture of the groundmass. They are angular, broken, often with molten edges. In Shutov's classification [25] terrigenous clastic rocks are feldspar-quartzose graywackes. The total thickness of the suite is 1000 m.

The Botakara suite (Table 3) is widespread in the southeastern Kokzhot block. Near the Ters and Botakara Rivers, Argybetsai Gorge, and other localities, gradual transitions of this suite from lower to higher sediments is observed.

At the lower part of the bed the suite appears as a rhythmic alternation of light-gray small-grained limestone (maximum thickness of layers 8 cm) with green argillite (up to 1.5 cm). Pyrite crystals occur throughout the rock (5-10, sometimes 20 mm). The sequence of layers in the carbonate-clay cyclites is the following (bottom to top): limestone with silt grain size and a minor amount of clay matter with normal gradational sorting of clastic material; micritic limestone with abundant clay material; and green argillite.

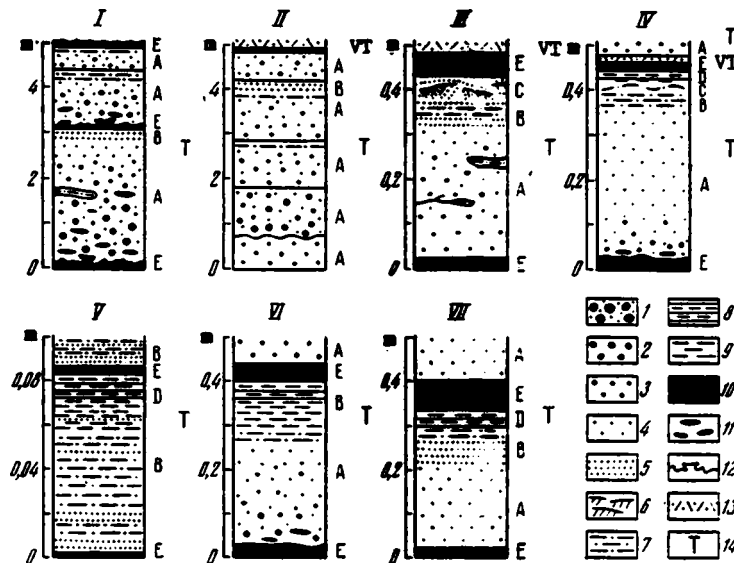


Fig. 5. Flysch cyclites: terrigenous sand-clay sediments of Kuyuk suite (I-IV), Konurtobe suite (VI-VII), limestone Botakara suite (V): (1) rubble sandstone, gritstone, clay intraclasts (matrix: sand-silt-pelite); (2-4) sandstone (2 - coarse-grained, 3 - medium-grained, 4 - small-grained); (5) sorted sandstone; (6) thin-layered sandstone; (7) silty sandstone and sandy siltstone; (8) thin intrastratification of siltstone and argillite; (9) siltstone; (10) argillite; (11) argillite intraclasts; (12) layer base mechanoglyphs; (13) volcanic tuff; (14) genetic sediment types. T = turbidites with intervals of Bouma's turbidite model (A, B, C, D, E); VT = volcanic tuff.

These features are typical for turbidite stream deposits and similar to the characteristics of the clastic rocks of the lower suite of the Kokzhot series. This suggests that the sediments of the carbonate suite are also a peculiar variety of turbidite flow deposits. These sediments are frequent on the slopes of modern reefs and carbonate rises, such as Bagam [23]. The carbonate material was apparently provided by nearly contemporaneous Tamda series of the Lesser Karatau. The sediments of the Botakara suite in that case are elements of the peripheral distal parts of deep-sea fans. Interlayers of small-grained limestone with obliquely wavy stratification are also observed; they were formed as a result of rewashing by bottom flows of previously deposited material. At the very top of the suite carbonate rocks give way to dark-gray, black, very small-grained and microgranular varieties, which supersede argillite completely. Their formation is associated with the vertical precipitation of carbonate ooze and its later alteration. The apparently permanent general carbonate accumulation background seems to be overshadowed by the influx of clastic matter. The disappearance of carbonate turbidites from the section indicates a change of the landscape, such as a leveling of the relief in the supply carbonate province or its submersion. The total thickness of the suite is 150-200 m.

The Konurtobe suite (Table 4) is widespread in the basins of the Ulken, Kishkene Baka and Ters Rivers near Konurtobe Mountain. It appears as a rhythmic alternation of dark-green gray small-, medium-, and less often, coarse-grained sandstone, siltstone, and argillite. The rock fragments are similar in their mineral composition to the sediments of the Kuyuk suite. The rhythm in rock alternation, however, is here less pronounced. Cyclites are found: sandstone, sandstone-argillite, and sandstone-siltstone-argillite. The sand element of the cyclites is predominant (20-50 cm thick). The sandstone beds are either massive or with gradation from medium- to small-grained psammite to coarse-grained silt varieties, with turbidite sequences A, ABE, AE, and less often ABDE. The lower contacts of the cyclites are sharp-wavy and slightly erosional; the top contacts are sharp or gradual. Bed base signs are typical. We interpret these accumulations as derivatives of turbidite flows within the middle fan of the deep-sea eluvial cones. The silt-argillite interlayers interstratified

with them have a horizontal, less often oblique, wavy layering and are interpreted as ~~inter-~~ turbidite sediments. The thickness of the suite is 350-400 m.

The data thus indicate that the Kokzhot suite consists mainly of sediments of autokinet-ic flows (mainly turbidite, less often grain flows). Contourites and sediments of calm (pelagic) sedimentations are also found. The Kokzhot series must have been formed in rela-tively deep-sea settings. Figure 5 shows the various structural types of turbidite cyclites. Terrigenous and carbonate turbidites are distinguished. All are characterized by the same regularity in the structure of the section. They can also be observed in plan. It is the normal gradational distribution of material in all structural types; it is seen in the gen-eral decrease of the granulometric sizes from the base to the roof of cyclites, accompanied by an improved sorting and changes of the bed base and internal structural signs.

The interval A (the principal gradational element) is represented by granulometric types of rocks ranging from small gravel to sandy siltstone. A poor sorting of material, large amounts of the clay matrix, and interformational conglomerates are the typical features.

The B, C, and D intervals consist of small-grained sandstone and sandy and clayey silt-stone. The B and D layers are the lower and upper laminar grain elements with fine horizon-tal stratification or layering, good sorting, and unclearly expressed normal gradation. In the interval D a higher clay content and a poor definition in the section are reported. The interval C, located between B and D, displays a microoblique stratification in section. The upper interval E is not stratified; it consists of green clay argillite of a carbonate-silicic-chlorite-sericitic composition, probably with a fine admixture of ash.

Background sediments are distinctly identified in the Kuyuk suite, where they are rep-resented by ash tuff. An analysis of the stucture of sections of the genetic types, as de-fined by the granulometric composition of sediments, the textural and structural features (poor processing and weak sorting, especially of the lower interval; and gradational distri-bution of material), the variety of stratification patterns, the hieroglyphs of mechanogenic and biogenic origin, and the submarine slump structures suggest that this carbonate-terrigen-ous formation is flyschoid. Dark microgranular limestone at the top of the Botakara suite is the only exception; we consider it to be an allophilic member of this formation [24].

The sedimentation conditions in the flysch paleobasin are similar to the sedimentation settings in passive near-continental margins of the Atlantic type.

LITERATURE CITED

1. A. A. Abdulin, G. Kh. Ergaliev, and Zh. S. Sargaskaev, "Vendian-Lower Paleozoic," in: Geology and Metallogeny [in Russian], Vol. 1, Nauka, Alma-Ata (1986), pp. 29-34.
2. L. N. Botvinkina, Methodological Guide to Studies of Stratification [in Russian], Nauka, Moscow (1965).
3. N. B. Vassoevich, "On flyschoid structures (signs)," Tr. Lvov. Geol. o-va, Ser. Geol., No. 3, 17-85 (1953).
4. N. B. Vassoevich, Flysch and Methods of Its Study [in Russian], Gostoptekhizdat, Lenin-grad-Moscow (1948).
5. N. B. Vassoevich, Flysch Formation Conditions [in Russian], Gostoptekhizdat, Leningrad-Moscow (1951).
6. I. A. Vyltsan, Flyschoid Formations [in Russian], Tomsk Univ. (1978).
7. O. S. Vyalov, "A brief essay on the flysch of the Carpathians and its characteristics," Tr. Lvov. Geol. o-va, Ser. Geol., No. 1, 43-61 (1948).
8. V. N. Grigor'ev, "Sedimentation of edaphogenic material," in: Geosynclinal and Oceanic Sedimentation and Volcanism [in Russian], Nauka, Moscow (1984), pp. 24-37.
9. V. A. Grossgeim, "The significance and method of study of hieroglyphs (with special reference to the Caucasus flysch)," Izv. Akad. Nauk SSSR, Ser. Geol., No. 2, 111-120 (1946).
10. G. Kh. Ergaliev, Zh. S. Sargaskaev, S. P. Koneva, and T. B. Baitorina, "On the age of the Kokzhot series of the Lesser Karatau," Vestn. Akad. Nauk KazSSR, No. 1, 43-45 (1987).
11. B. M. Keller, "Flysch formation of the Paleozoic in the Zilair synclinorium in the South Ural and similar formations," Tr. GIN Akad. Nauk SSSR, No. 104 (1949).
12. A. P. Lisitsyn, Sedimentation in Oceans [in Russian], Nauka, Moscow (1974).
13. A. P. Lisitsyn, Processes of Oceanic Sedimentation [in Russian], Nauka, Moscow (1978).
14. V. V. Longvinov, Essays on Ocean Lithodynamics [in Russian], Nauka, Moscow (1973).

15. I. O. Murdmaa, "Edaphogenic clastic sediments in recent oceans," in: *Paleontology and Marine Geology: The Geological Congress, 25th Session, Papers Presented by Soviet Geologists* [in Russian], Nauka, Moscow (1976), pp. 256-265.
16. V. P. Petelin, "Formation of the mineral composition of deep-sea sediments," in: *The History of the World Ocean* [in Russian], Nauka, Moscow (1971), pp. 207-219.
17. F. Pettijohn, *Sedimentary Rocks* [Russian translation], Nedra, Moscow (1981).
18. Ge. E. Reinach and I. B. Singh, *Terrigenous Sedimentation Environments* [Russian translation], Nedra, Moscow (1981).
19. *Survey Guide to Excursions 045A and 101A* [in Russian], Kazakhstan, Alma-Ata (1984).
20. V. T. Frolov, *Genetic Classification of Marine Sediments* [in Russian], Nedra, Moscow (1984).
21. V. T. Frolov, *Practice and Methods of Comprehensive Stratigraphic-Lithological and Paleogeographical Studies* [in Russian], Moscow State Univ. (1965).
22. I. V. Khvorova, "Surface structures in the Carboniferous and Lower Permian flysch of the South Ural," *Tr. GIN*, No. 155, 136-155 (1955).
23. I. V. Khvorova, "Principal traits of sedimentation in the Paleozoic geosynclinal basins and comparisons with sedimentation in recent oceans," in: *Geology of the World Ocean, 27th International Geological Congress, Vol. 6, Part I* [in Russian], Nauka, Moscow (1984), pp. 3-8.
24. N. S. Shatskii, "Geological formations and sedimentary minerals," in: *Selected Works*, Vol. 3 [in Russian], Nauka, Moscow (1965).
25. V. D. Shutov, "Classification of sandstones," *Litol. Polezn. Iskop.*, No. 5, 86-104 (1967).
26. A. H. Bouma, *Sedimentology of Some Flysch Deposits: A Graphic Approach to Facies Interpretation*, Elsevier, Amsterdam (1962).
27. R. L. Folk, "Practical petrographic classification of limestones," *Bull. Am. Assoc. Petrol. Geol.*, 43, 1-38 (1959).
28. R. G. Walker, "Deep-water sandstone facies and ancient submarine fans: Models for exploration for stratigraphic traps," *Bull. Am. Assoc. Petrol. Geol.*, 62, 932-966 (1978).

POST-SEDIMENTARY TRANSFORMATIONS OF MIDDLE PLIOCENE CLAYS OF THE SOUTH-CASPIAN DEPRESSION

L. A. Buryakovskii, R. D. Dzhevanshir,
M. B. Kheirov, and R. Yu. Aliyarov

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The interaction of thermobaric and hydrochemical factors on the process of post-sedimentary transformation of middle Pliocene clays of the South-Caspian depression is studied on the basis of experimental geologic-geophysical and geochemical investigations. Correlations are obtained of montmorillonite content with pore pressure, temperature, and the mineralization of pore fluids of the chlor-calcic and hydrocarbonate-natric types. A conclusion was drawn on the possible formation of authigenic montmorillonite at great depth.

Clay rocks and the fluids contained in them are important indicators of trends in processes of post-sedimentary transformations. First, the clay minerals which appear in the composition of clay rocks are extremely sensitive to thermobaric factors. Second, clay sequences are accumulations of very unusual gas-water fluids, which also determine the degree and character of the catagenic transformation of every sedimentary sequence [17].

The noted questions have a special value for young sedimentary basins, which are characterized by the presence of thick, rapidly accumulating clay sequences. A vivid example

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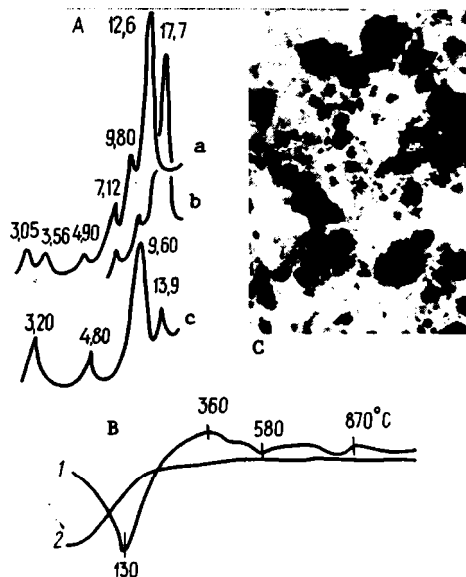


Fig. 1. Diffractograms (A), thermogram (B), and electron photomicrograph (C), characteristic for clays of South-Caspian depression with AHPP (Bulla-more, well 38, depth 6183-6186 m). a) air-dry state; b) after saturation with glycerin; c) after heating to 580°C (numbers on curves are given in angstroms). 1) differential heating curve; 2) loss of weight.

is the South-Caspian depression, which is distinguished by a diverse and rather unique association of parameters; an exceptionally high rate of sediment accumulation (up to 1.3 km/million years); a huge (up to 25 km) thickness of sedimentary cover and its Quaternary-Pliocene completion (up to 10 km); sand-silt-clay type of sediments; anomalously high pore pressure (average coefficient of anomaly up to 1.8); low heat flow and layer temperatures (at depths on order of 6 km the temperature is ~100-110°C); an inverted character of the hydrochemical profile (succession with depth of chlor-calcic and chlor-magnesian waters into hydrocarbonate-natric waters); and wide development of mud volcanism. Clays and clay rocks make up from 50 to 95% of the section and play a key role in the formation of the lithologic-mineralogic, geochemical, and thermobaric characteristics of the basin [3, 4].

It was established by investigators in [15] that the fine-pelitic fraction of clays in Tertiary deposits of the South-Caspian depression are composed primarily montmorillonite and hydromicas (Fig. 1), whose total content reaches 60-80%. The remaining portion occurs as chlorite, kaolinite, and mixed layered clay formations of the montmorillonite-hydromica and montmorillonite-chlorite series with disordered alternation of layers. Most interesting and important from a theoretical and practical viewpoint is the exceptionally high stability of montmorillonite at great depths in the indicated deposits. Thus, in the region of the Bakinsk archipelago, at depths on the order of 6 km and greater, the content of this mineral reaches an average of nearly 40%, reaching 75% in individual samples. This increases interest in the study of factors explaining such a low level of post-diagenetic transformation of clay rocks.

Catagenesis of rocks and transformation of clay minerals are a complicated process, proceeding over long geologic time under the influence of interrelated and interdependent natural factors. It is therefore a problem of extreme difficulty to recognize the effects of each of these, that is, to give a quantitative estimate of the intensity of the influence of one or another factor. The most natural path for its solution is the formulation of experimental investigations on both artificial samples with given properties, and on core material. However the great complexity and duration of similar experiments frequently does not permit the achievement of the formulated goal. Thus, for example, experiments studying the influence of anomalously high pore pressures (AHPP) on the transformation of clay minerals were not conducted in practice, to say nothing of consideration of the entire complex of thermobaric and geochemical factors. In such conditions, one of the paths towards solution of considered problem is the utilization of data from the detailed study of the composition and structural features of clay minerals, with inclusion of the complex of contemporary methods of mineralogical investigation, performed on a representative collection of clay samples from an actual stratigraphic interval.

The primary objects of our investigation were clay rocks from the productive sequence (PS) of middle Pliocene deposits from the central and western borders of the South-Caspian depression. Significant factual material has accumulated on these deposits, consisting of results of investigations into clays and clay minerals over a wide interval of depths, up to 6.2 km (more than 5000 diffractometric, thermographic, electron-microscopic, and other

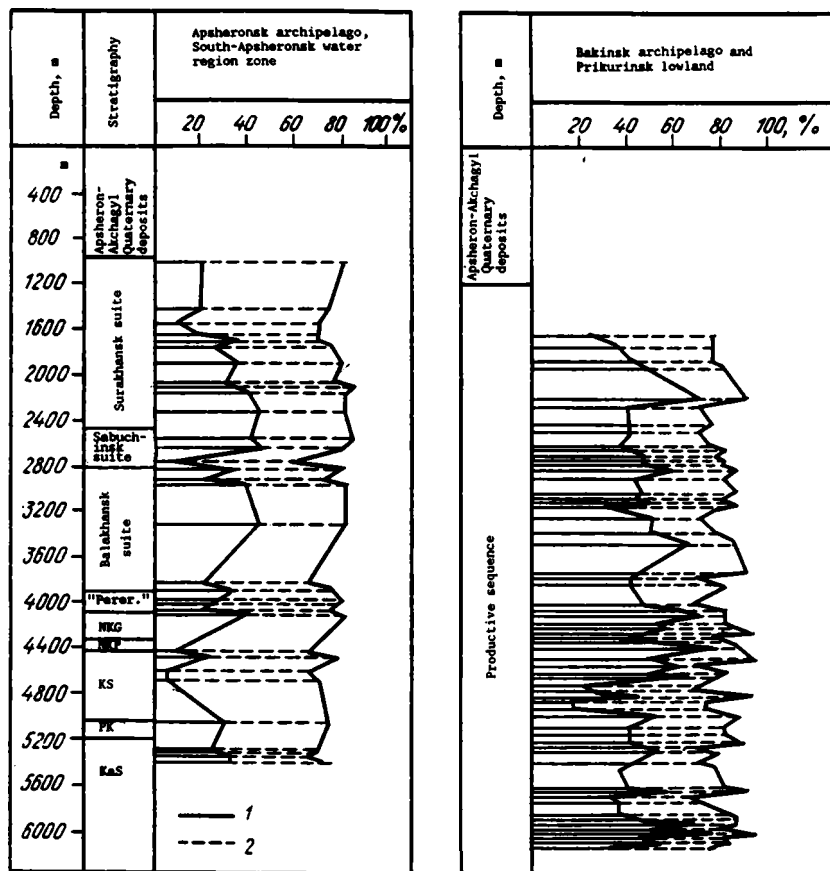


Fig. 2. Montmorillonite (1) and hydromica (2) content in the finely pelitic fraction of middle Pliocene clays. a) Apsheronsk archipelago, South-Apsheronsk water area zone; b) Bakinsk archipelago and Prikurinsk lowland.

forms of analysis). Statistical processing of these data made it possible to recognize a series of features in the character of clay mineral distribution both in regional plan and by depth.

In Fig. 2 are presented diagrams of montmorillonite and hydromica contents in sections of occurrences from the Apsheronsk archipelago (Neftyanye Kamni-2, Gryazevaya Sopka, Yuzhnaya-2, 28 April), the South-Apsheronsk water region zone (Bazhar), the Bakinsk archipelago (Sangachaly-more-Duvannyi-more-Bulla island, Bulla-more, Alyaty-more, Khamamdag-more, Garasu, Sangi-Mugan', Kamen' Persiyanina), and the Prikurinsk region (Kyurovdag, Karabagly).

Clay rocks from occurrences of the Apsheronsk peninsula and similar types of archipelago are primarily of hydromica composition. The hydromica content (H) averages 48%, while the montmorillonite content (M) is 24% (see Fig. 2), that is, $M/H = 0.5$. The section of these occurrences is quite inhomogeneous in clay mineral contents. The montmorillonite content varies from 5 to 40%, in few cases reaching 45%, while hydromica content ranges from 20-60%. Data from x-ray diffractometric investigations of clays for various suites of middle Pliocene deposits from the Apsheronsk peninsula and the adjacent water region are generalized in Table 1. As is seen, in the upper series of the productive sequence, the Surakhansk and Sabunchinsk suites are characterized by the largest content of montmorillonite (31 and 35% respectively), while in the Balakhansk suite the montmorillonite content decreases to 21.4%. In the lower series of the PS, the largest montmorillonite content (30%) is noted at the NKG and Kalinsk suites.

In occurrences of the Bakinsk archipelago and the Prikurinsk region, the montmorillonite content in clay rocks (41%) somewhat predominates over the hydromica content (37%); $M/G = 1.1$. In distinction from the region of the Apsheronsk peninsula and the adjacent water area, the section is on the whole characterized by a more stable mineral composition (see Fig. 2), preserving a significant amount of swelling clay minerals in its section.

TABLE 1. Mineral Contents in Clays of the Apsheronsk Peninsula Occurrence and Archipelago, %.

Suite, horizon	Mont- moril- lonite (M)	Hydro- mica (H)	M/H	Suite, horizon	Mont- moril- lonite (M)	Hydro- mica (H)	M/H
Upper series of the pro- ductive sequence				Lower series of the productive sequence			
Surakhansk	10—45 31,0	35—60 46,3	0,67	NGK	25—35 30,0	30—40 41,3	0,73
Sabunchinsk	25—45 35,0	35—40 37,5	0,93	KS	10—30 20,0	40—60 50,0	0,40
Balakhansk	10—40 21,1	40—55 50,6	0,42	KaS	10—40 30,0	40—60 47,0	0,67

Note. In Tables 1 and 2, the limits of the contents are shown in the numerator, and the averages are shown in the denominator.

One of the causes of the observed distribution of clay minerals connects both the different sources of detrital material input for the separate portions of the sediment accumulation basin and the predominantly allothigenic occurrences of clay minerals, and the variations in the rate of material intake in the process of sediment accumulation. The Russian platform, the Kilyazi-Krasnovodsk uplift, an island existing north of Apsheron, as well as the south-eastern slope of the Greater Caucasus served as the primary source regions for terrigenous material for the Apsheronsk peninsula and the adjacent water region of the Caspian Sea. Weathering of more ancient (Mesozoic-Paleogene) magmatic and sedimentary rocks from complexes of the mountain massifs of the Greater and Lesser Caucasus, and Talysh served as the primary source for the Prikurinsk region and the Bakinsk archipelago [1, 11].

For a study of the effects of hydrochemical and thermobaric factors on the post-sedimentary alteration of Pliocene clays in the considered region, literature and background data of chemical analyses of layer waters and measurements of layer temperatures [2, 10] were generalized, in addition to our own investigations into the determination of pore pressures in clays by methods of industrial geophysics (Table 2).

As is known, the hydrochemical environment in a basin of sediment accumulation has significant influence on the intensity of post-sedimentary transformation [17]. Therefore, first it is important to ascertain the nature of the hydrochemical regime observed in the Cenozoic complex of the South-Caspian depression, namely: whether it is a consequence of the catagenesis of clay rocks and the transformation of clay minerals, or it is formed predominantly as a result of the action of other factors. In this connection, the problem presenting the greatest interest is the origin of the invested hydrochemical profile in the section of the South-Caspian depression, that is, of succession of deep chlor-calcic waters by little mineralized hydrocarbonate-natric waters. A series of investigators explains the cause of this phenomenon by interformational return flows of fluids through a system of tectonic nonconformities and by mixture in different volume proportions of syngenetic sedimentogenic chlor-calcic solutions with little mineralized hydrocarbonate-natric waters of Jurassic-Valanginian generational provenance [2].

The phenomenon of hydrochemical inversion is also established in other regions. As E. F. Stankevich [13] showed, hydrocarbonate type waters are most characteristic for young sedimentary basins. The presence of dissolved organic material in sediments also has great value. I. S. Gramberg [7] established that in such conditions, pore waters are already enriched in bicarbonate natra at stage of diagenesis, and they transform to hydrocarbonate-natric type. In this connection, the development of alkali-hydrocarbonate natric waters in the South-Caspian at great depths is completely understandable, where the section still contains a significant volume of dissolved organic material [3]. In addition, we have recently obtained quite numerous data from laboratory and industrial observations, indicating that a decrease in the mineralization of waters, with succession of chlor-calcic waters by alkali hydrocarbonate-natric waters is more characteristic for the zone of AHPP development.

G. Chilingar and G. Rieke III [19] performed an experiment on the compression confinement of samples composed of a mixture of montmorillonite and hydromica (50/50) saturated with sea water. Distillation of the squeezed out water was observed in the process of continuous

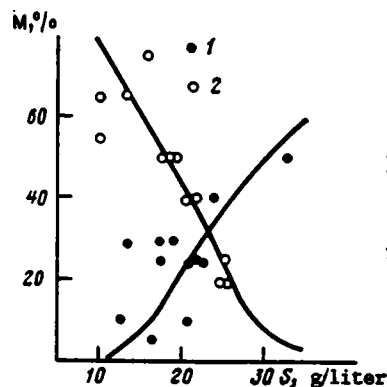


Fig. 3. Dependence of montmorillonite content on layer water salinity. 1) hydrocarbonate-natric; 2) chlor-calcic.

growth of sealing and pore pressure. The appearance of hydrochemical inversion in zones of AHPP is recorded in a section of the Dnepr-Donets depression, where a decrease in the total mineralization of waters with depth and succession of the chlor-calcic type of waters by hydrocarbonate-natric waters was noted [12]. A clear tendency towards a decrease in the mineralization of layer waters in horizons with AHPP is noted in the Prichernomorsk-Krymsk gas-oil bearing district of the southern Ukraine; at the same time it is established that waters of hydrocarbonate-natric type are characteristic here for terrigenous deposits with AHPP [9]. Analogous data on the decrease of layer water salinity with increase of pressure are also noted in the Gulf of Mexico region [14].

In view of this assertion, it is evident that the appearance of hydrochemical inversion in the section of the South-Caspian depression may be explained by genetic connection of the hydrochemical regime with the development of anomalously high pore pressures in clays. As seen from the data presented in Table 2, the most intense AHPP zones are characteristic for regions of the Bakinsk archipelago and Prikurinsk region, where the waters are primarily hydrocarbonate-natric.

Thus, it is possible to assume that hydrochemical features of the section are caused by internal processes and are determined mainly by the features of compaction of clay rocks and squeezing out of pore waters. In their turn, the hydrochemical factors influence the process of catagenetic transformation of clay minerals.

Shown in Fig. 3 are the graphs we constructed of the dependence between montmorillonite content and the total mineralization of the layer waters for the two types of pore solutions which are characteristic for the occurrences of the South-Caspian depression: chlor-calcic and hydrocarbonate-natric. As seen, a direct connection is observed for the hydrocarbonate-natric waters, that is, with increase in their mineralization, the conditions for preservation of montmorillonite are improved and its content in the clays is increased. Increase of the total mineralization of these waters is caused by growth of the fraction of carbonate and hydrocarbonate salts of alkali and alkali-earth metals. Sections of the Bakinsk archipelago and the Prikurinsk oil-gas bearing region, as well as rocks from the lower series of the productive sequence of Apsheronsk peninsula and adjacent water regions, that is, regions and sections in which the clay rocks are characterized by increased montmorillonite content, are characterized by hydrocarbonate-natric composition of the waters.

Regarding chlor-calcic waters, their connection with the montmorillonite content is inverse. The chloride content increases with an increase in the salinity of these waters, in particular sylvite (KCl).

As is seen, an alkali medium is favorable for the formation and preservation of montmorillonite. This is also confirmed by results of computer geochemical modeling [8].

A program in PL-1 language for the ES computer was utilized, which was analogous to the geochemical model for an IBM type computer proposed in [20]. The program makes it possible to model the equilibrium distribution of a majority of elements present in the pore solutions at temperature intervals up to 350°C on the basis of data on the chemical composition of layer waters, temperature, pH and Eh. For determination of the possibility of dissolution or restoration from solution of one or another mineral, calculation of values of the difference of Gibbs free energy (ΔG) for the studied conditions and equilibrium conditions is specified in the program.

TABLE 2. Clay Mineral Contents, Pore Pressure Gradients, and Geothermal Gradients in Areas of South-Caspian Depression

Area	Clay mineral content, %					Pore pressure gradient, MPa/m	Geothermal gradient, °C/km
	M	H	C	Ch	mixed layer		
Bibi-Eibat	tr.—30	40—65	10—30	tr.—5	tr.—5	0,0125	28,5
	17	33	26	3	1		
Gryazevaya Sopka	10—35	45—60	20	tr.—5	tr.	0,135	26,0
	24	51		3,8			
28 April	40	40	15—20	tr.	tr.—5	0,0146	24,0
			17,5		2,5		
Bakhar	10—55	30—55	15—25	tr.—10	tr.—5	0,166	28,0
	27,7	46,1	20,4	4,2	0,8		
Sangachaly-more-Duvan-nvi-more-Bulla island	5—60	5—60	tr.—20	tr.—15	tr.—5	0,0171	16,0
	41	39	13	6	1		
Bulla-more	5—70	5—70	tr.—35	tr.—10	tr.—10	0,0182	16,0
	39	37	16	4	4		
Alyaty-more	45—50	25	15	5	5—10	0,0178	16,0
	47				8		
Khamdag-more-Kamen' Ignetiya island	30—75	10—45	10—15	tr.—10	tr.	0,0176	16,0
	49	28	12,5	5			
Kyurovdag, Karabagly	40—75	10—35	tr.—20	tr.—15	—	0,0176	16,0
	53	25	12	10			

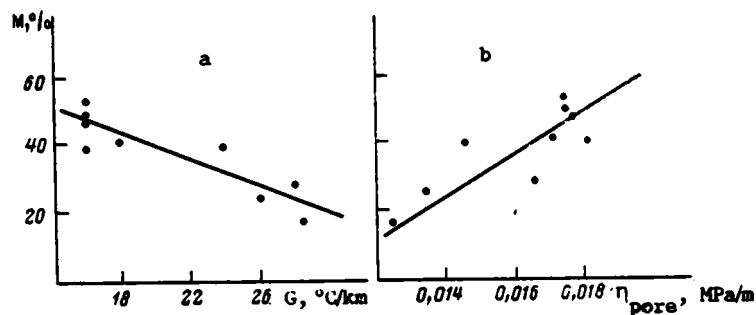


Fig. 4. Dependence of montmorillonite content on the geothermal gradient (a) and the pore pressure gradient (b).

TABLE 3. Reference Data on the Chemical Composition of Layer Waters from the Bakinsk Archipelago Utilized in Modeling

Element	Concentration, mg/liter	Element	Concentration, mg/liter
Cl ⁻	709,0	Ca ²⁺	8,02
SO ₄ ²⁻	211,2	Mg ²⁺	2,44
HCO ₃ ⁻	195,2	Na ⁺ + K ⁺	618,7
CO ₃ ²⁻	36,0	Al ³⁺	0,005—0,1
RCOO ⁻	17,7	SiO ₂	70,0

Data on the chemical composition of layer waters of the archipelago at depths on the order of 4-4.5 km were utilized (Table 3) [8, 10].

The temperature was equal to 85°C, and the magnitude of pH for the studied conditions averaged 7.0-7.5. As a result of computer variance calculations, it was established [8] that in the interval of pH variation from 4 to 9 and greater, the values of ΔG for hydromica are always less than zero, which indicates the impossibility of restoration of the given mineral from solution.

Together with this, in the interval of pH variation from 5 to 9, the values of ΔG for Ca-, Mg-, and Na-montmorillonites are either greater than zero, or close to zero, which indicates the possible formation of montmorillonite from solution. As is seen, the geochemical conditions at great depths in the Bakinsk archipelago not only assist in the preservation of allothigenic montmorillonite, but also permit us to propose the possible transformation of hydromica into montmorillonite, with formation of secondary montmorillonite.

Another factor assisting in the transformation of montmorillonite is the thermal regime of the medium [16, 18, 21]. A temperature increase accelerates the process of montmorillonite degradation, while this in its turn favors its catagenetic transformation into nonswelling minerals (hydromica and chlorite). In this connection, sections with high geothermal background should be characterized by a small montmorillonite content.

A graph is presented in Fig. 4a, of the dependence of montmorillonite content on the geothermal gradient in clays of the middle Pliocene of the South-Caspian depression. The greatest montmorillonite contents are found in the clays of the Bakinsk archipelago and Prikurinsk region, which are characterized by a low geothermal gradient (16°C/km). The Apsheron peninsula occurrence and the adjacent water areas, having a higher (24.0-28.5°C/km) geothermal gradient, are characterized by smaller montmorillonite contents (see Table

Since the reaction of transformation of montmorillonite into hydromica proceeds with the elimination of interlayer water, then conditions for which desorbing water withdraws from the pore space without hindrance will be favorable for the development of this process. Therefore every factor opposing the withdrawal of fluids from the interlayer space of the clays may lead to retardation or further stoppage of the reaction of transformation of montmorillonite into hydromica or chlorite. In [6] was shown that such a factor is anomalously high pore pressure. In this connection it is possible to assume that in the studied region a direct dependence must exist between montmorillonite content and the intensity of AHPP development.

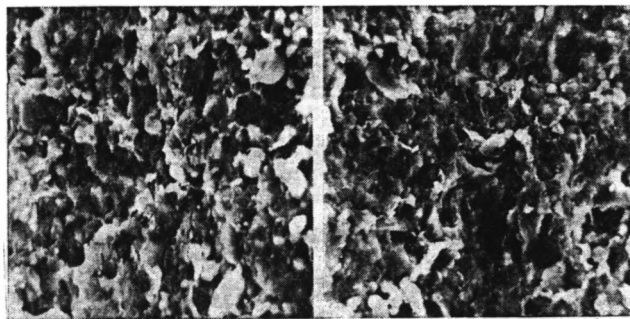


Fig. 5. Photomicrographs of surfaces of cleavage of clay samples obtained by the SEM method (Bulla-more, well 15, depth 5128-5132 m), $\times 1000$.

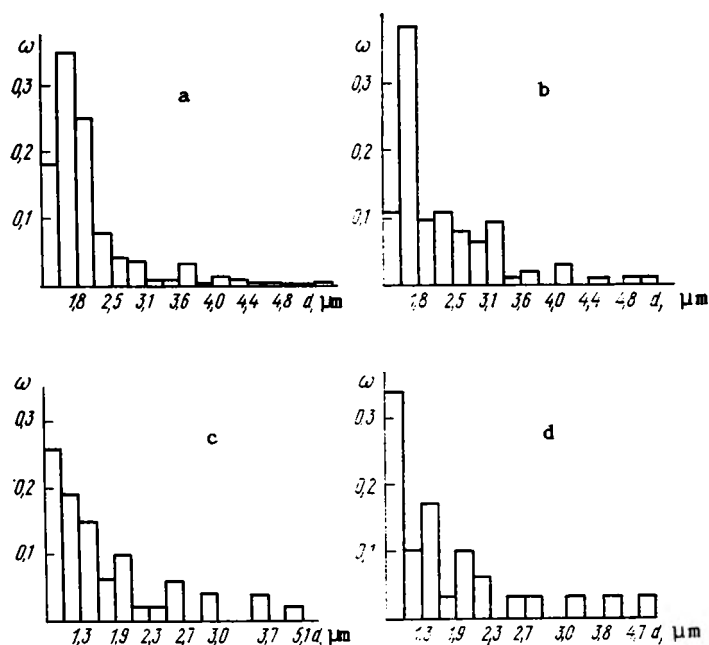


Fig. 6. Histograms of the distribution of particle diameters for primary (a, c) and secondary (b, d) montmorillonite (Bulla-more, depth 5128-5132 m). (a, b) $\times 1000$, (c, d) $\times 3000$. ω is relative frequency.

Shown in Fig. 4b is the dependence between the montmorillonite content and the pore pressure gradient in clays. As is seen, the connection between these parameters is rather close. In regions of the Bakinsk archipelago and the Prikurinsk lowland, characterized by intense development of AHPP (pore pressure gradients of 0.018-0.019 MPa/m), the montmorillonite content in clays in the section of an average reaches 53%. In regions with moderate development of AHPP (the Apsheronsk archipelago, the South Apsheronsk water region zone), the montmorillonite content decreases to 17%.

From this discussion it may be seen that rather close correlations between the clay mineral content and the thermobaric and hydrochemical features of the section are established in the South-Caspian depression. In addition, it is evident that all these parameters interact, and the stability of montmorillonite at great depths depends mainly on them. Moreover, in the section of the Bakinsk archipelago at depths greater than 4-5 km, formation of secondary montmorillonite from hydromicas [6] is recorded in scanning electron microscope (SEM) data. Such a phenomenon is explained by the influence of relatively low temperatures, anomalously high pore pressures, and the alkali composition of pore waters enriched in ions of Mg^{2+} , Na^+ , and Ca^{2+} .

The derivation of the numerical characteristics of the particles (or more likely aggregate accumulations) of primary and secondary montmorillonite at great depths is

TABLE 4. Numerical Characteristics of Particle Sizes for Montmorillonite in the Finely Pelitic Fraction of Clay Rocks from the Bulla-More Occurrence

Photo-graph, No.	Magnifi-cation	No. of meas.	Interval value d, μ	Median d_{Me} , μm	Av. diam., $\bar{d}$, μm	Diver-gence, σ_d , μm	Vari-ation V_d , %	Asym-metry, A
Primary montmorillonite								
6402, 6405, 6401, 6404	1000	296	0,9—11,2	1,9	2,6	3,3	127	0,58
	3000	46	0,5—5,1	1,5	1,9	2,1	112	0,53
Secondary montmorillonite								
6402, 6405, 6401, 6404	1000	118	0,9—6,5	2,0	2,7	2,9	107	0,70
	3000	29	0,6—4,8	1,6	1,9	2,2	116	0,52

TABLE 5. Montmorillonite Content from SEM Data, %.

Photograph number	Magnifi-cation	Montmorillonite		Total	Portion of secondary
		primary	secondary		
6401	3000	14,5	7,1	21,6	32,9
6402	1000	13,5	6,5	20,0	32,5
6404	3000	10,5	5,4	15,9	34,0
6405	1000	14,3	5,2	19,5	26,7

interesting. Such an approximate estimate may be achieved by means of a corresponding quantitative analysis of SEM data. With this goal, we utilized photomicrographs of surfaces of two shears from a clay sample from the 5128-5132-m interval of the Bulla-more occurrence (Fig. 5). The photos were subjected to measurements performed on parallel and stratal shears, where the relations between primary and secondary montmorillonite are seen most clearly. For this we utilized photos with magnifications of 1000 and 3000, which permitted us to control the exactness of the performed estimate to a determined degree.

The results of the statistical processing of the data on measurements of particle diameters for primary and secondary montmorillonite are shown in Table 4. As seen, the particle sizes for primary montmorillonite are found within the limits of 0.5-11.2 μm , while the secondary sizes range from 0.6-6.5 μm . The average value of the particle diameters for the primary and secondary montmorillonite roughly coincide. Some difference in the results of analysis of photos with magnification of 1000 and 3000 times is explained by the fact that in the photos with a magnification of 3000 times it is possible to record a greater number of fine particles, which naturally yields a somewhat smaller value of the diameters (Fig. 6).

As seen from data presented in Fig. 6 and Table 4, the distributions of particle diameters are right-asymmetric, close to lognormal. In all four cases, the average arithmetic values of the grain diameters exceeds the median by 0.3-0.7 μm . It is significant that sizes of montmorillonite particles appeared rather close to the sizes of the pores, which was established earlier by SEM data [5].

Utilizing the obtained data, we performed an estimate of the primary and secondary montmorillonite content (Table 5). On average, the total montmorillonite content in relation to the entire area of the photomicrographs reached 19.2% (the primary forms 13.2% and the secondary 6% of that number). The montmorillonite fraction reached an average of 31.5% of the total mass. This indicates a rather high intensity for the process of secondary montmorillonite formation from hydromica at great depths.

A specific feature of the postsedimentational transformation of middle Pliocene clays of the South-Caspian depression is the retardation of the process of transformation of montmorillonite into hydromica or chlorite at great depths, and the replacement of this process by the process of transformation of hydromica into swelling minerals of the montmorillonite group. These processes occur on a background of lowered thermal and increased baric activity at depth, and are closely connected with them. It is possible to assume that the inverted

hydrochemical profile of the studied deposits is a consequence of interaction of the transformation of clay minerals with thermobaric conditions at depth, owing to the fact that pore solutions are distilled in the process of clay sediment compaction. The obtained result indicates development in the South Caspian depression of the process named elisional catagenesis by V. N. Kholodvii.

LITERATURE CITED

1. A. A. Ali-Zade, É. A. Daidbekova, and M. B. Kheirov, "Composition and genetic nature of clay minerals of oil-gas bearing deposits of Azerbaidzhan," *Izv. Akad. Nauk AzSSR, Ser. Nauk Zemle*, No. 4, 22-40 (1971).
2. A. R. Akhundov, U. Sh. Mekhtiev, and M. Z. Rachinskii, *Handbook on Underground Waters of Oil-Gas and Gas-Condensate Occurrences of Azerbaidzhan* [in Russian], Maarif, Baku (1976).
3. L. A. Buryakovskii, I. S. Guliev, and R. D. Dzhevanshir, "Prediction of oil-gas bearing at great depths in Cenozoic sedimentary-rock basins," in: *Oil-Gas Formation at Great Depths, Thesis Proceedings of the 5th All-Union Seminar* [in Russian], Nauka, Moscow (1986), pp. 133-134.
4. L. A. Buryakovskii, I. S. Dzhaferov, and R. D. Dzhevanshir, *Prediction of the Physical Properties of Reservoirs and Covers of Oil and Gas* [in Russian], Nedra, Moscow (1982).
5. L. A. Buryakovskii and R. D. Dzhevanshir, "Pore space structure in Cenozoic clays of Azerbaidzhan in connection with development of anomalously high pore pressures in them," *Litol. Polezn. Iskop.*, No. 1, 96-105 (1985).
6. L. A. Buryakovskii and R. D. Dzhevanshir, "The interrelation and interference transformations of clay minerals with thermobaric conditions at depth," *Geokhimiya*, No. 4, 512-521 (1986).
7. I. S. Gramberg, *Paleohydrochemistry of Terrigenous Sequences (Exemplified by Upper Paleozoic Deposits of Northern Central Siberia)* [in Russian], Nedra, Moscow (1973).
8. R. D. Dzhevanshir, "Modeling geochemical conditions of the inversion process of clay mineral transformation (Bakinsk archipelago)," *Izv. Akad. Nauk AzSSR, Ser. Nauk Zemle*, No. 5, 137-142 (1985).
9. N. Ya. Kunin and O. M. Ozernii, "Geochemical anomalies in AHPP zones of the southern Ukraine," *Geol. Nefti Gaza*, No. 3, 8-12 (1985).
10. Sh. F. Mekhtiev, M. Z. Rachinskii, and G. A. Poloudin, "Distinguishing features of layer waters in oil and gas-condensate deposits of the productive sequence of Western Apsheron, Southeastern Kobystan, the Bakinsk archipelago, and the northeast portion of the Prikurinsk lowland," *Izv. Vyssh. Uchebn. Zaved., Neft' Gaz*, No. 6, 7-12 (1970).
11. I. S. Mustafaev, *Lithofacies and Paleogeography of middle Pliocene Oil-Gas Bearing Deposits of the Caspian Depression* [in Russian], Azerneshr, Baku (1963).
12. R. M. Novosiletskii and D. V. Sharin, "Hydrogeochemical characteristics of the AHPP and DDV diffusion zone," *Geol. Nefti Gaza*, No. 7, 42-46 (1982).
13. E. F. Stankevich, "On the connection of underground hydrocarbonate-natric waters with the processes of oil formation," in: *Hydrogeological Criteria for Appraisal of Oil and Gas Bearing Prospects of the Russian Platform* [in Russian], BelNIGRI, Minsk, pp. 97-103 (1971).
14. U. Kh. Fertl', *Anomalous Layer Pressures* [Russian translation], Nedra, Moscow (1980).
15. M. B. Kheirov, "The effect of the deposition depth of sedimentary rocks on the transformation of clay minerals," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 8, 144-151 (1979).
16. N. I. Khitarov and V. A. Pugin, "Montmorillonite under conditions of increased temperature and pressures," *Geokhimiya*, No. 7, 790-795 (1966).
17. V. N. Kholodov, "Advances in the knowledge of catagenesis, Report 2," *Litol. Polezn. Iskop.*, No. 5, 15-32 (1982).
18. J. F. Burst, "Diagenesis of Gulf Coast clayey sediments and its possible relation to petroleum migration," *Bull. Am. Assoc. Petrol Geol.*, 53, 73-93 (1969).
19. G. V. Chilingar and H. Rieke, "III. Chemistry of interstitial solutions in undercompacted (overpressured) versus wellcompacted shales," *Proc. Internat. Clay Conf., Appl. Publ. Ltd., Wilmette, Illinois*, 673-678 (1975).
20. J. K. Kharaka and H. Barnes, "Solmineq-solution-mineral equilibrium computations," *USGS Computer Cont., Nat. Techn. Inf. Rept.*, PB-215-583 (1973).
21. M. C. Powers, "Fluid-release mechanisms in compacting marine mudrocks and their importance in oil exploration," *Bull. Am. Assoc. Petrol Geol.*, 51, 1240-1254 (1967).

SUBDIVISION OF ZONAL METAMORPHIC PRECAMBRIAN COMPLEXES ACCORDING
TO CLASTOGENIC ACCESSORY MINERAL ASSOCIATIONS

A. G. Valasis, B. A. Gornostai,
and A. P. Kazak

UDC 551.71/72

Original data are reported from a study of clastogenic accessory minerals of the zonal metamorphic Upper Precambrian complex of the Payo ridge (Kanin Peninsula). The results of an area sampling of metasedimentary rocks are used to identify the sets of accessory minerals; mineralogic associations are determined by statistical analysis and the indicator mineral forms are identified. Criteria are formulated for separating authigenic and clastogenic minerals in metamorphic rocks. The results allow isolating the Tarkhanov and Tabuev series; they confirm a monoclinical overall structure of the complex and disprove the possibility of its eugeosynclinal genesis.

Separation and stratigraphic correlation of ancient metamorphic complexes and sections are important aspects of Precambrian geology. The task is especially difficult in conditions of zonal metamorphism and poorly exposed regions, where direct lithologic and petrographic observations cannot be used to determine the actual relationships of rock strata and sets. Associations of accessory minerals studied in combination with traditional lithologic methods are valuable in such circumstances.

The investigations of the metamorphic complex of the Kanin Peninsula, where our method of area mineralogic mapping was tested, had been started back in 1902 by F. N. Chernyshev; until recently, however, there has been no commonly accepted stratigraphic scheme of the Precambrian. A tripartite division, suggested by Getsen [2], is the most familiar scheme. It separates the Mikulkin, Tarkhanov, and Tabuev series.* Dividing and correlating the sections of the sedimentary-metamorphic rocks is difficult because of intense dislocations, the uneven degrees of metamorphism of the primary sedimentary rocks, and their limited exposure.

In addition to lithologic and facies descriptions, we conducted area mineralogic investigations of accessory mineral sets so as to construct the stratigraphic subdivisions of this region.

Among the various lithologic rock types - metapsammites, metasilstones, and metapelites - metamorphosed in various regional metamorphic facies, we selected 10-15 kg core samples and isolated from the heavy mineral fraction for binocular investigation; at the same time, rocks were studied in polished sections. Mineralogic investigations of metamorphic strata determined that they contained large quantities of detrital accessory minerals, such as zircon, garnet, apatite, staurolite, disthene, sillimanite, ilmenite, rutile, leucosene, pyrite, sphene, tourmaline, epidote, glaucophane, amphibole, pyroxene, olivine, moissanite, ruby, pyrope, and meteorite spheres. In studies of accessories, one needs criteria and features for distinguishing between authigenic minerals formed in rocks by postsedimentary metamorphic processes, on the one hand, and allothigenic (i.e., clastogenic or detrital) minerals, on the

*The subdivisions of the Riphean are based on the degree of metamorphism - from amphibolitic to greenschist facies - and the structural position of the beds. The oldest (Mikulkin) series was metamorphosed in the PT-conditions of the amphibolite facies and forms a dome-shaped core.

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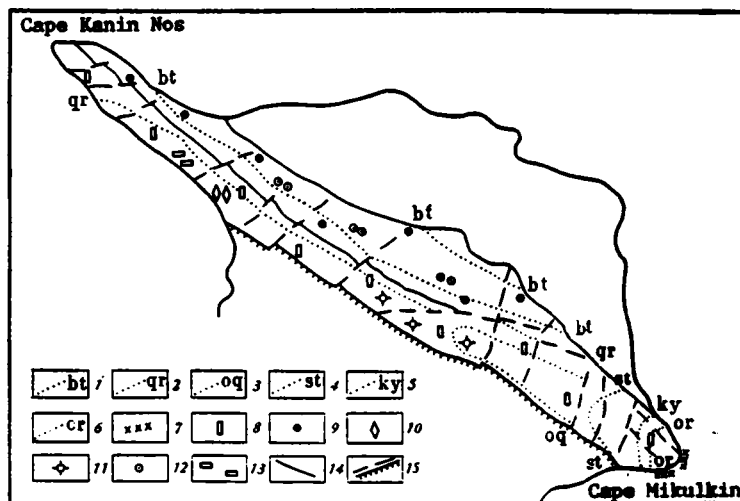


Fig. 1. A schematic map of the occurrence of clastogenic zircon and the positions of the isolines of indicator minerals of the metamorphic complex of Payo ridge: (1-6) isolines (1 - biotite, 2 - garnet, 3 - oligoclase, 4 - staurolite, 5 - kyanite, 6 - orthoclase); (7) pegmatite veins in the zone of the amphibolite facies; (8) yellow zircon of Tarkhanov series; (9) pink zircon of Tabuev series; (10, 11) clastogenic grains (10 - pyrope, 11 - moissanite); (12) meteorite spheres; (13) metamorphosed ancient rutile placers; (14) boundary between Tarkhanov and Tabuev series; (15) tectonic faults.

other [3, 6]. We use the following features to identify detrital minerals: 1) a degree of rounding of mineral grains and rough surfaces with traces of transport, such as furrows and drag scratches, strokes, or matte texture; 2) the correspondence of the mean grain size of clastogenic minerals to the rock granulometry, which is an important feature in studies of metapsammitic rocks; 3) a prohibited association of accessory and rock-forming minerals (for example, disthene or pyroxene in rocks metamorphosed in the setting of a biotite-chlorite subfacies) means unequivocally that they are clastogenic; and 4) finds of rare minerals (such as pyrope, moissanite, or meteorite spheres in sedimentary metamorphic rocks) indication that these are allothigenic.

For the diagnosis of authigenic minerals the features include the absence of rounding and idiomorphic grains, the correspondence of minerals with the rock-forming parageneses, the similarities of inclusions in accessory and rock-forming minerals, and a variety of specific features applicable to specific situations.

Two stratigraphic subdivisions were identified from studies of detrital accessory minerals in the Riphean: the "lower" series and the "upper" series. In each series, a set of accessory minerals has been isolated; we statistically determined the mineral association and defined the indicator mineral forms (Fig. 1).

The lower Tarkhanov series consists of terrigenous rock beds, with a subordinate presence of carbonate layers. In the northwestern part, members of terrigenous flysch are interstratified with metasiltstone, flyschoid horizons, and carbonate shallow-sea flysch; in the southeastern block, where the Mikulkin series was described previously, the stratified section consists of metasiltstone-pelite, terrigenous flysch, and horizons of intraformational conglomerate. The primary sediments in the southeastern block thus appear as a facially altered sections of central and northwestern blocks, but do not constitute a lithologically isolated subdivision. Generally, coarse clastic sediments are typical for the lower series, which is underscored by the morphology of the detrital minerals. Formationally, the sediments of the Tarkhanov series correspond to the upper portion of the terrigenous formation, as described by Belousov [1]. The overall formation thickness is 4000 m.

The primary sedimentary rocks of the Tarkhanov series are metamorphosed in various regional metamorphism facies - from PT-conditions of the biotite-chlorite subfacies to the

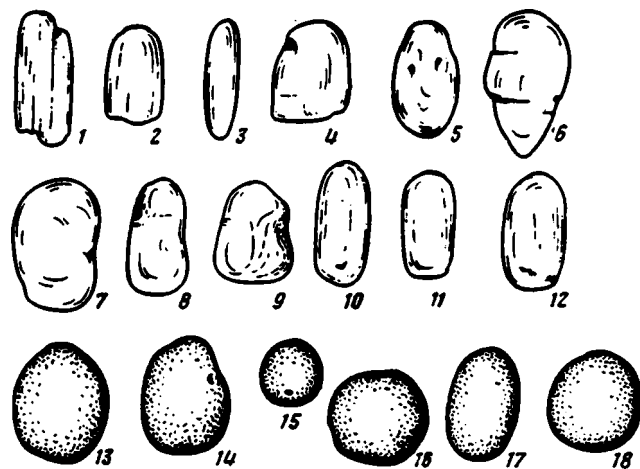


Fig. 2. Clastogenic zircons: (1-6) light, light-yellow, and colorless poorly rounded zircons of the southeastern block (Mikulkin suite, bottom of the Upper Proterozoic); (7-12) gray, yellowish, and colorless with yellowish tinge poorly rounded zircons of the Tarkhanov series; (13-18) light-pink and dark-pink well-rounded zircons of the Tabuev series.

amphibolite facies. Despite the uneven degree of metamorphism, a common zircon-apatite association of clastogenic minerals is established for the series. The correlating minerals are zircon, apatite, garnet, and rutile. Besides these minerals, clastogenic amphibole and pyroxene are common; of the rare accessory minerals, there are pyrope and moissanite, not described by previous investigators. Zircon has been identified as the indicator mineral.

Various amounts of zircon are present in all lithologic rock types. Its contents vary substantially from traces to hundreds of grams per ton. The highest zircon contents are described in metapsammitic horizons, where the relative concentration in a sample varies within several tenths of a percentage point. The zircon is almost colorless, with a characteristic yellowish tinge. It is poorly rounded; sometimes the grains are angular, rarely retaining the crystallographic shapes. Distinct scratches and drag furrows are seen on all grains. The zircon from the southeastern part of the section is represented by more angular grains (Fig. 2, 1-12), which are less rounded.

The upper series, identified by the set of accessory minerals and described by Getseva as the Tabuev series [2], differs from the Tarkhanov series in its composition. The bottom of the section is formed of deep-sea flysch (turbidite formations) and terrigenous-carbonate sediments; the top of the section is represented by diverse phyllites and roofing slates with metapsammitic interlayers of a varying thickness.

A formational analysis of the primary sedimentary rocks suggests that the Tabuev series consists of terrigenous-carbonate and slate-molassoid formations, 3600 and 2800 m thick, respectively.

The Tabuev sedimentary rocks were metamorphosed in conditions of a sericite-chlorite and biotite-chlorite subfacies. A zircon-garnet association of accessory minerals has been identified for them.

The correlating minerals are zircon, garnet, leucosene, amphibole, and magnetite. Chrome-diopside, omphacite, and meteorite spheres are also widespread in the sections.

Zircon is present in all lithologic varieties, but its contents vary. The highest concentrations (up to hundreds of grams per ton) are observed in metapsammitic horizons of the section top. The zircons are of a characteristic pink, dark-pink, or bright crimson color. The grains are well rounded, with round and spheroid shapes being predominant. A characteristic feature is the matte surface of some of the grains, a consequence of being transported for a long time (Fig. 2, 13-18).

The set of accessory minerals of the upper Tabuev series is distinct from the accessory set of the Tarkhanov series in the following respects: first, the indicator series in the

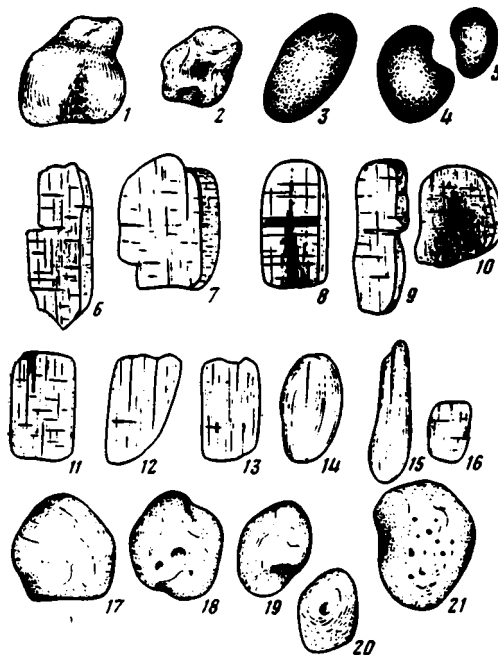


Fig. 3. Accessory clastogenic minerals: (1-5) well-rounded terrigenous staurolite; (6-7) poorly rounded terrigenous disthene; (8-10) same, with inclusion of graphitic material; (11) rounded terrigenous monoclinic pyroxene; (12-16) rounded terrigenous amphibole; (17-21) well-rounded terrigenous garnet.

following respects: first, the indicator mineral (zircon) is of a different type; second, detrital minerals (such as garnet, pyroxene, magnetite, and leucoxene) are more widespread, while the amount of clastogenic mineral (apatite, rutile, and ilmenite) is limited; and, thirdly, the set contains minerals such as glaucophane, chrome diopside, omphacite, and meteorite spheres, while terrigenous rocks are entirely devoid of disthene, staurolite, pyrope, and moissanite.

Some of the accessory minerals are briefly described below.

Garnet. In the Riphean rocks of the Payo ridge both allothigenic and authigenic garnet are common. The highest concentrations of detrital grains are observed in the rocks of the Tabuev series, where they are sometimes as high as 400 g/t. The following varieties of clastogenic garnet are distinguished: 1) purple-pink ($N = 1.800-1.820$); 2) yellowish-pink and brownish-yellow; 3) orange and orange-pink ($N = 1.800$); and 4) pink and light-pink ($N = 1.790-1.810$). Most garnet grains are well rounded, sometimes perfectly rounded. Some of the grains show traces of intense dissolution with characteristic etching figures; the good rounding and the furrows and scratches of dragging observed in all forms leave no doubt as to their clastogenic genesis (Fig. 3, 17-21).

Terrigenous pink garnet of the Tarkhanov series typically contains inclusions of various minerals - amphibole, biotite, and opaque inclusions of ore minerals (Fig. 3, 21).

Authigenic garnet is typical for Tarkhanov rocks. It associates paragenetically with neomorphous minerals, such as biotite and staurolite. It is represented by pink-gray varieties, with well-expressed crystallographic forms. The refractive index of authigenic garnets is much lower (1.770-1.776) than in allothigenic varieties. Other distinctive features are the opacity of the grains and numerous biotite, muscovite, and quartz inclusions.

Here is the composition of authigenic garnet, based on one chemical analysis, %: SiO_2 38.70; TiO_2 0.99; Al_2O_3 20.43; Fe_2O_3 2.30; FeO 27.90; MnO 1.58; MgO 3.35; CaO 4.20; Σ 99.55.

Disthene. Authigenic and allothigenic varieties are distinguished. The mineral is typical for Tarkhanov rocks; the relative proportions in the specimens from the bottom of the section are as high as 20%. Terrigenous disthene is usually colorless; some of the grains

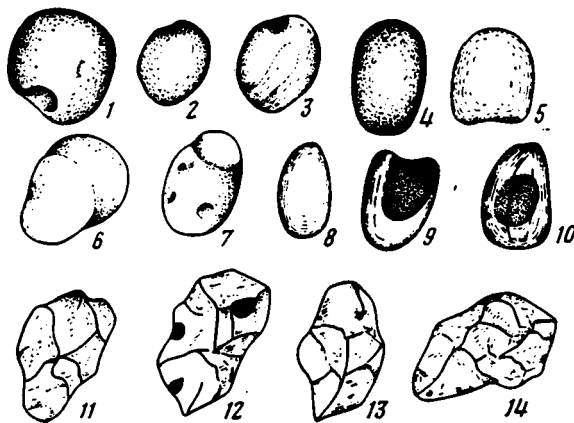


Fig. 4. Allothigenic and authigenic apatite: (1-8) rounded terrigenous apatite; (9-10) same, with gray cores; (11-14) authigenic apatite of an irregular lumpy texture.

contain numerous inclusions of an opaque carbon material, which imparts a grayish coloring to the disthene (Fig. 3, 3). Some of the grains are elongate and prismatic; more often, they are tabular and exhibit uneven degrees of rounding. Due to the distinct transverse cleavage some grains have ledge-shaped forms with surfaces that have been smoothed (Fig. 3, 6-10).

Authigenic disthene is found only in the southeastern block, where the rocks were metamorphosed in an environment of an amphibolitic facies in paragenesis with neomorphous minerals. This disthene is characterized by pronounced crystallographic forms and has a characteristic blue color. Some of the authigenic disthene was apparently formed by recrystallization of clastogenic varieties.

Staurolite. Like with garnet and disthene, the Tarkhanov rocks clearly fall into two genetic types: authigenic and allothigenic staurolite. The relative content of clastogenic grains in the heavy fraction specimen is 10%. Their colors are orange, yellow, and reddish brown. Staurolite is found as rounded varieties. Grains range in diameter from 0.5 to 1.5 mm (Fig. 3, 1-5).

Authigenic staurolite is found only in the southeastern part of the section; its grains are angular and have a characteristic yellowish-brown color.

Apatite. Apatite is a common accessory mineral of the Tarkhanov series. The highest apatite content is found in the bottom parts of the section and in the southeastern block, where 10-15% of specimens are apatite. Two genetic and three morphologic types of the mineral are distinguished (Fig. 4, 1-8).

The clastogenic apatite is grayish and well rounded; isolated grains have a well-polished surface. Clastogenic polished apatite displays prismatic and short-prismatic patterns with furrows and scratches of dragging and contains "core" inclusions, coloring it gray and dark gray (Fig. 4, 9-10).

Authigenic apatite is perfectly transparent, with single grains containing biotite and amphibole inclusions. Morphologically, authigenic apatite is represented by lumps and angular grains (Fig. 4, 11-14).

Rutile. Rutile is found in the Tabuev and Tarkhanov series; in the latter, it consists of two genetic types. In the Tarkhanov series, clastogenic rutile content in selected meta-sandstone horizons is as high as 1 kg/t, which can be classified as low-grade metamorphosed paleoplacers.

Allothigenic rutile of the Tarkhanov series consists of elongate prismatic black grains with smoothed edges, i.e., of a poor rounding. A small number of much better rounded dark brownish and yellowish-red rutile are also found.

Authigenic rutile was mostly formed by dissolution and recrystallization of clastogenic rutile and Ti-containing minerals in an environment of epidote-amphibolitic and amphibolitic metamorphism facies. A regular increase in authigenic rutile content is observed in those

specimens where the concentrations of clastogenic grains is also higher. Authigenic rutile is usually found as columnar prismatic grains, rugged twins, or amorphous growths, which may also be an indication of recrystallization of terrigenous rutile in the course of metamorphism.

Glaucophane. Glaucophane is described for the first time; it is found in the rocks of the Tabuev series. Clastogenic grains are of a prismatic, short-prismatic, or columnar form with smoothed and well-rounded edges. In polished sections, the mineral displays a characteristic pleochroism: N_g - dark blue (1.648); N_p - purple (1.642).

* * *

The study of accessory clastogenic minerals from the Upper Proterozoic of the metamorphosed beds in Payo ridge (Kanin Peninsula), combined with lithologic and petrographic descriptions, suggests certain conclusions relating to the stratigraphy and structure of this region and the primary nature of the metamorphosed rocks. It becomes possible to reconstruct the paleogeographic sedimentation environments in the region.

1. The Tarkhanov and Tabuev series are distinctly identified by accessory mineral sets: according to mineralogic and formational data, the Mikulkin stratigraphic entity can be isolated in this area only in the rank of a suite. The mineralogic sets clearly fix the stratigraphic boundary, which in geological terms is the dividing line between terrigenous and terrigenous-carbonate formations. The succession of these formations in the section, in turn, was determined by a change of the tectonic conditions. A regular variation of the morphology of clastogenic minerals and the fact that accessory sets do not recur in the section indicate a predominantly monoclinic rock occurrence, which is fully supported by structural studies.

2. The area sampling of lithologic rock types has indicated the presence of clastogenic minerals in all petrographic varieties of the profile. Metagabbroids and sedimentary-volcanic formations, described earlier [2], when subjected to detailed petrochemical, lithologic, and mineralogic investigations, were found to be typical sedimentary formation. The "basic orthorocks" in the Predovskii's reconstructive diagrams falls within the "overlap" fields, but occupy a distinct lithologic position in the section (they occur at the roof of the cyclothem with a gradational transition within the metapsammitic basement) and contain typical detrital zircon and disthene. These data indicate a highly limited occurrence of volcanogenic rocks in the Precambrian of the Payo ridge, indicating the absence of a eugeo-synclinal regime during the formation time of the Riphean strata in that region.

3. Mineralogic studies of terrigenous accessory minerals and lithologic-facies investigations can be used for retrospective reconstructions and description of the sedimentation settings in the paleobasin.

The sea transgression that presumably began during the Burzyanian epoch advanced from the northeast and the east (as evidenced by the poorest rounding of allothigenic minerals in the southeastern block). Clastics were transported from the southwest, as confirmed by the widespread oblique stratified series at the bottom of the section, documenting a northeasterly direction of terrigenous material, where the denudation area contained crystalline rocks similar to the rock set of the Kaive series. The close paragenetic association of pink garnet with disthene, staurolite, and aegirine, and the paragenesis of orange garnet with amphibole and ilmenite, show that their source was crystalline alumina, garnet staurolite, garnet-disthene schists, and garnet-containing amphibolites or metagabbroids. At the same time, kimberlite rocks were eroded, as indicated by pyrope and moissanite in ancient sediments. During that stage of transgression, shallow-sea and subflysch sediments were deposited; the denudation area was not farther than 100 km away, as documented by the widespread large grains of minerals unstable to mechanical erosion (such as disthene, andalusite, pyroxene, and others).

The next stage of transgression, during the Yurmantinian epoch, was associated with active tectonics; it resulted in an abrupt change of the facies and accumulation of deep-sea turbidite and carbonate-terrigenous sediments. Far from the coastline, pink zircon, garnet and other clastogenic minerals with a high degree of rounding were deposited in the rocks of terrigenous-carbonate and slate-molassoid formations. Sedimentary strata were formed from washed-out ancient ophiolites, eclogitic rocks, and glaucophane schists, which supplied terrigenous minerals (such as chrome diopside, omphacite, glaucophane, and others). During

the Karatavian time, the transgression was apparently succeeded by regression, the ancient basin became shallow, and molassoid beds (represented by psammite, siltstone, and roofing and coaly slates) were deposited. There were no intense tectonic movements during that stage, because the set of accessory minerals remained unchanged, meaning that the relationship of sedimentation and denudation regions was the same. On the other hand, the slightly metamorphosed sedimentary rocks exhibit no structural features (oblique and wavy stratification, internal rewashing, etc.) that would indicate an active hydrodynamic setting. This is further evidence of a shallow-sea lagoon facies that determined the accumulation of terrigenous coaly sediments.

4. The sets of clastogenic accessory minerals are diagnosed correctly and correlate in metamorphic rocks of all phases of regional metamorphism; despite a partial regeneration in the amphibolitic facies of even a conservative mineral such as zircon, they are all characterized by good preservation of the indicator forms. Detailed studies of detrital minerals help resolve complicated issues in Precambrian geology, such as stratigraphic subdivisions and correlations, the description of the genesis of metamorphic rocks (their membership in the para- or the orthoserries), the description of structural features of the sets, and the reconstruction of primary sedimentation conditions and the paleotectonic environment of the region.

The method of mineralogic area mapping of the associations of clastogenic minerals combined with conventional lithologic and facies studies can be recommended as an effective tool for stratigraphic division and geologic mapping of Precambrian complexes.

LITERATURE CITED

1. V. V. Belousov, Basic Problems of Geotectonics [in Russian], Gosgeoltekhizdat, Moscow (1962).
2. V. G. Getsen, The Basement Structure of Northern Timan and the Kanin Peninsula [in Russian], Nauka, Leningrad (1975).
3. A. A. Kukharensky, Mineralogy of Placers [in Russian], Gosgeoltekhizdat, Moscow (1961).
4. T. F. Negrutsa, V. Z. Negrutsa, and A. P. Kazak, "Evaluation of the paleogeographic conditions in the Middle Proterozoic sedimentogenesis of Karelia, based on an analysis of accessory minerals," in: Lithology and Sedimentary Geology of the Precambrian: Tenth National Lithologic Conference [in Russian], Izd. Akad. Nauk SSSR, Moscow (1973), pp. 150-151.
5. N. A. Plaksenko, I. N. Shchegolev, and V. V. Il'yash, "Division of metamorphic Archean beds according to the sets of accessory minerals," Geol. Zh., 38, No. 2, 32-41 (1978).
6. N. P. Shcherbak, N. Yu. Levkovskaya, and N. I. Polovko, "Clastogenic zircons and monazites of metamorphic rocks of the Ukrainian Shield as criteria for rock age and genesis," in: Problems of Precambrian Geology [in Russian], Nedra, Moscow (1975), pp. 181-189.

SECONDARY ALTERATION OF BASIC VOLCANIC GLASSES IN ALKALINE
BASALTOIDS OF THE CHANCHAR SUITE (SOUTH URAL)

M. N. Il'inskaya

UDC 552.14:552.323.5(243.853)

The paper reports on the results of a study of alteration of basic volcanic glasses by modern instrumental methods with a scanning electron microscope (Stereoscan-600) and an x-ray spectral microanalyzer (Camebax). The alteration of the initial silicate melt has been described in detail, including the patterns of its differentiation and partial recrystallization.

Volcanic activity, and especially its effects on sedimentation and metallization in recent oceans and seas, continues to attract the interest of investigators. Solid, liquid, and gaseous volcanic products participate in sedimentogenesis. The boundary relations are particularly important in situations where seawater or sedimentary and volcanogenic components interact and affect one another. These influences are hard to analyze; they belong to the most well-masked phenomena that do not lend themselves to easy observation.

In the past few years, attention has been paid to details of the structure, composition, and occurrence of volcanic, volcanogenic-sedimentary, sedimentary rocks and sediments, and products of their alteration in samples collected from the ocean floor. Massive data from research studies in the Soviet Union and other countries allowed undertaking these investigations on a large scale. They include a detailed analysis of volcanic glasses of a basic composition. Hyaloclastics of various granulometry are widespread in oceanic sediments, with which they mix in uneven proportions. The origins of these hyaloclastics are associated with desquamation of a silicate melt effused into cold bottom water during the formation of pillow lavas and the rapid cooling (chilling) of the melt. Hyaloclasts usually fill interstices between spheres and pillows and are carried out submarine currents over large areas, far from the sites of volcanic activity.

Fragments of basic volcanic glass are highly unstable and are usually altered soon. Initially, palagonite, montmorillonite, and mixed-layer chlorite-montmorillonite entities are mainly formed after these glasses. The clay minerals developed after hyaloclastites correspond to certain eupelagic clays [6].

Detailed data on palagonite formed after sideromelane have been reported by Geptner [1]. The author notes that at the moment there is no consensus as to the composition and formation environments of palagonite; however, he draws the important conclusion that its genesis is directly related to the solution of important lithologic problems. The palagonitization of volcanic glass in various physicochemical settings involves the migration of silicon, calcium, magnesium, sodium, and potassium from the glass, oxidation of ferrous iron, and intrusion of water into the glass structure [1].

Detailed studies of the processes involved in the alteration of volcanic glasses have been undertaken at the Geological Institute of the USSR Academy of Sciences by Kossovskaya et al. [5], Khvorova and Voronin [7], Kudryavtsev [4], and other investigators. The studies are usually conducted on conjugate pairs: glass-palagonite, glass-zeolite, glass-hydrotalcite, and glass-smectite. Other variants are likely to be found.

The alteration of isotropic volcanic glass to a series of anisotropic stratified micaceous or zeolitic and other minerals is a complex and not fully understood process. Usually

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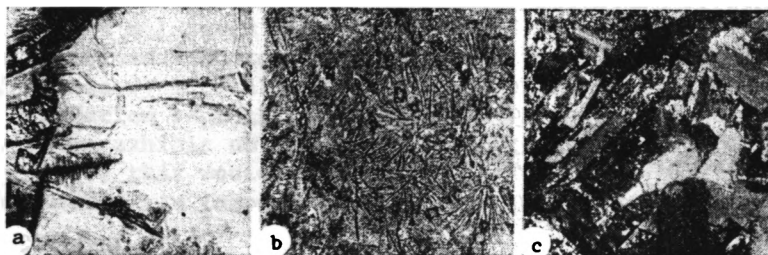


Fig. 1. Potassium trachyandesitobasalts with different degrees of crystallization: (a) volcanic glass from chilling crust with rare crystallites; polished section, magnification 160x without analyzer; (b) variolite; polished section, magnification 20x without analyzer; (c) holocrystalline rock from the core of a pillow lava; polished section, magnification 20x, crossed nicols.

TABLE 1. Composition of Potassium Trachyandesitobasalts, Volcanic Glasses, and Crystallites, wt. %

Component	1	2	3	4	5	6	7	8	9	10	11
SiO ₂	50.34	52.76	52.33	54.35	52.63	35.93	44.60	50.63	37.07	62.88	29.51
TiO ₂	0.89	0.68	0.82	0.36	0.79	0.29	1.29	0.96	4.87	0.24	35.30
Al ₂ O ₃	14.53	16.39	16.01	18.95	17.22	13.99	11.75	5.07	16.28	19.59	5.95
FeO	8.81	7.18	6.61	2.57	7.42	21.11	9.86	7.21	17.59	0.45	1.04
MnO	0.11	0.08	0.10	0.07	0.09	0.20	0.15	0.07	0.14	0.03	Her
MgO	3.21	4.01	4.23	0.40	2.99	15.37	10.49	14.42	13.03	0.07	»
CaO	7.09	4.68	4.43	5.64	6.18	1.28	20.91	21.62	0.14	1.21	25.70
Na ₂ O	2.83	2.27	2.69	0.14	0.01	0.03	0.42	0.31	0.39	1.99	Her
K ₂ O	1.51	5.48	7.16	1.64	0.48	0.31	0.07	0.07	7.84	10.65	0.07
H ₂ O ⁺	8.42	4.05	2.23	—	—	—	—	—	—	—	—
H ₂ O ⁻	1.23	1.10	1.49	—	—	—	—	—	—	—	—
P ₂ O ₅	0.26	0.41	0.44	—	—	—	—	—	—	—	—
Sum	99.23	99.17	98.51	84.12	87.81	88.50	99.54	99.90	97.35	97.11	97.57

Notes. (1-3) complete silicate analysis [2]; (1) volcanic glass (four specimens); (2) variolite (eight specimens); (3) holocrystalline rock (26 specimens); (4-11) results with micro-analyzer; (4) unaltered volcanic glass; (5) volcanic glass at the boundary with a thin crack; (6) strongly altered volcanic glass at the center of the crack; (7) hornblende; (8) pyroxene; (9) biotite; (10) orthoclase; (11) sphene. Analysis performed at the Geologic Institute, USSR Academy of Sciences.

we see the end result of secondary alteration; the intermediate stages of the redistribution of rock-forming oxides require extremely subtle analysis.

With the aid of scanning electron microscope and microanalysis of various models at the Laboratory of Physical Methods of Sedimentary Rock Studies of the Geological Institute, some of the specifics of the alterations have been revealed for the various geologic and petrochemical types of basalts and hyaloclastites associated with them, as found on the floor of Recent oceans and their older analogues confined to continents.

Remarkable data have been produced by a study of volcanic glasses from alkaline basaltoids confined to the Chanchar suite, widespread in the western slope of South Ural within the Sakmar zone. Korinevskii [3] and Zolotarev et al. [2] investigated rocks of an unusual composition that form the province of alkaline basaltoids. Korinevskii [3] isolated their biotitic varieties as a special type, called chancharite, after the Chanchar River, where they are fully represented and well-exposed in outcrops.

By their chemical composition and the set of rock-forming minerals, these are potassium trachyandesitobasalts. They belong to the Eifelian stage of the Middle Devonian and vary in thickness from 300 to 700 m. The crops of these rocks are traced in the meridional direction, on the sides of a large syncline in the watershed between Dambar and Chanchar, over 10-

15 km; the exposed portion is 1 to 2.5 km wide. The formation of these rocks coincides with the end of the volcanic activity in the region and the beginning of the epoch of consolidation of the folded elements.

The textural specifics of these rocks can be observed in the right bank cliffs on the Chanchar River. One sees clearly large isometric pillows, measuring up to 6 m across, and smaller rounded-flattened varieties. The interstices between the pillows are filled with hyaloclastic material, appearing as an unsorted mixing of angular fragments and shards of black volcanic glass. The pillows have a zonal structure. Under a vitreous chilling crust of the perimeter 5-15 cm thick a variolytic zone 40-50 cm thick is observed; toward the center of a pillow the degree of crystallization increases, and its core consists of fully crystalline rock (Fig. 1).

The magmatic melt from which potassium trachyandesitobasalt was formed experienced a series of transformations by the time of eruption. It became divided, as it were, into two constituents: the hydrated component and the relatively "dry" component. The hydrated component, containing up to 8-9% water, vitrified to an isotropic mass as it cooled; the less hydrated component, with a water content of at most 3-3.5%, recrystallized after eruption into a series of rocks of different texture but similar chemical composition. The parent magmatic melt was definitely rich in alkali (see Table 1) and intensely overheated. This is supported by the absence of intratelluric crystals; during a submarine effusion the melt was chilled abruptly and vitrified almost immediately. At the contact of overheated melt with cold water, extreme conditions were created, in which the hydrated portion of the magma vitrified rapidly and was subjected to desquamation, creating an immense mass of small hyaloclasts around a sphere chilled on the surface.

As was determined earlier [2], alkaline trachyandesitobasalt combines the geochemical features of the primitive oceanic tholeiitic series and some of the characteristics of the alkaline basalt series; its geochemical specifics reflect the processes of deep differentiation of liquational type [2].

The pillows that, as it were, floated in dense hyaloclast packing were peculiar, small and isolated, closed crystallization systems. This theory is confirmed by the fact that these pillow formations contain a holocrystalline structure at the core and that the rock-forming minerals include biotite and hornblende, which are typical for intrusive and subvolcanic rocks, because their formation requires volatile components (see Fig. 1c).

Potassium trachyandesitobasalt is remarkable for its high alkaline content (see Table 1, columns 2 and 3), amounting on average to 10%, with 7% contributed by potassium. Petrographic and chemical studies of these rocks were carried out separately for specimens from different structural zones of the isolated pillow immersed in the hyaloclast mass. The zones were found to differ not only in degree of crystallization but also in mineral and chemical composition. It was determined that volcanic glass is of a basic composition and contains much less alkalis, especially potassium, than the inner portions of variously crystallized pillows.

Volcanic glass from the pillow entities of Eifelian potassium alkaline basaltoids was studied in detail by petrographic and chemical analytic methods [2].

Petrographic study showed distinctly that the volcanic glass is isotropic and broken by a series of thin cracks to a pearlitic mixture (see Fig. 1a). It contains rare scattered small crystallites and microlites of leucocratic and mafic minerals, appearing as thin needles combined to spherulites and resembling a feather or spinifex structure.

Table 1 (column 1) gives the mean chemical compositions of volcanic glass for four specimens; the least altered varieties of volcanic glass with a control polished section were selected. The bulk analysis, however, determined average composition, because the glass contained inclusions of leucocratic and dark-green crystallites and products of secondary alteration, such as palagonite and smectite, that filled the dense net of minor cracks.

A more detailed investigation by the Laboratory of Physical Methods of Sedimentary Rock Studies with a scanning electron microscope (SEM) (Stereoscan-600 [Cambridge]) and an x-ray spectra microanalyzer (Camebax) yielded the characteristics of the compositions of unaltered and variously altered volcanic glass, as well as the data on the crystallites enclosed in the vitreous mass (see Table 1, columns 4-11).

Various degrees of glass alteration are clearly seen on the broken surfaces of volcanic

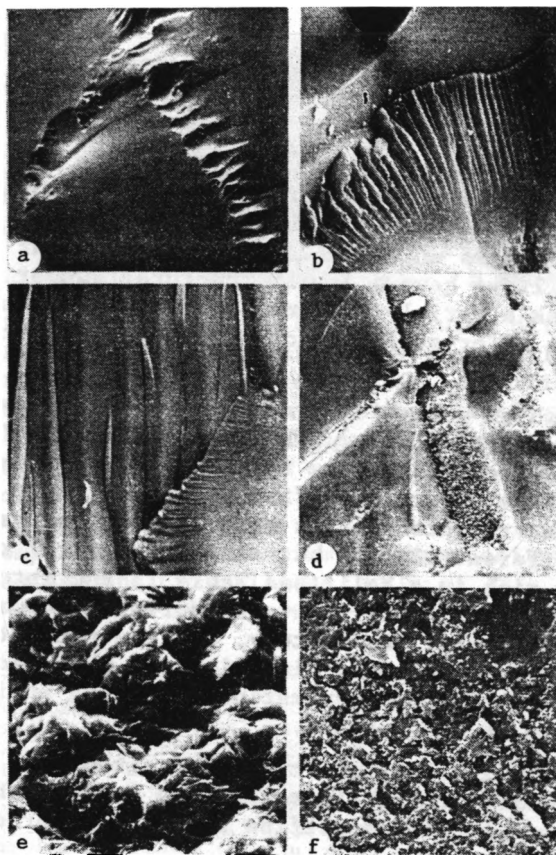


Fig. 2. Volcanic glasses and secondary alterations after them, photographed with a scanning electron microscope (by N. D. Serebrennikova with a Stereoscan-600 [Cambridge]): (a) unaltered glass, 5000 $\times$; (b) fissured, with a loosening zone (initial smectitization), 2000 $\times$; (c) longitudinal pores in volcanic glass formed after fissuring, 2000 $\times$; (d) smectitization developed after cracks and pores, 1000 $\times$; (e) montmorillonitization, 5000 $\times$; (f) smectitization along a crack, 5000 $\times$.

glass in the SEM with magnifications from 500 $\times$ to 5000 $\times$. The unaltered glass has a dense smooth surface with conchoidal fracture (Fig. 2a). The initial alterations appear as strong fissuring (see Fig. 2b) saturating the glass. In some segments, pores and small channels are seen (see Fig. 2c) with zones and cracks of loosening. Volcanic glass alteration involves partial crystallization of the initial silicate melt, with isolation of tiny microlites and crystallites (eutectics) (see Fig. 1a), as well as influx and removal of isolated components through a system of numerous cracks and pores, with participation of endogenous volatile components and heated seawater, which becomes reactive as it comes into contact with a hot silicate melt. Portions of unaltered glass and glass affected by secondary alteration (such as smectitization) are separated by sharp boundaries (see Fig. 2d), although gradual transitions sometimes can also be observed. On the broken surfaces along the cracks, where volcanic glass is fully altered, numerous flakes of diverse shapes are seen (see Fig. 2e,f).

Qualitative and quantitative characteristics of the chemical composition of volcanic glass have been obtained with a microanalyzer. The quantitative determinations of oxides were performed on three areas with different degrees of alteration: 1) in altered volcanic glass without cracks or inclusions; 2) at the boundary of unaltered volcanic glass and a thin crack filled with alteration products; and 3) at the center of a noticeable relatively wide ($\sim 1 \mu\text{m}$) crack, where volcanic glass is fully altered, probably to smectite. The results are given in Table 1 (columns 4-6). The table also includes the early determinations by the classical method of complete silicate analysis by the institute's analysis laboratory (see Table 1, column 1).

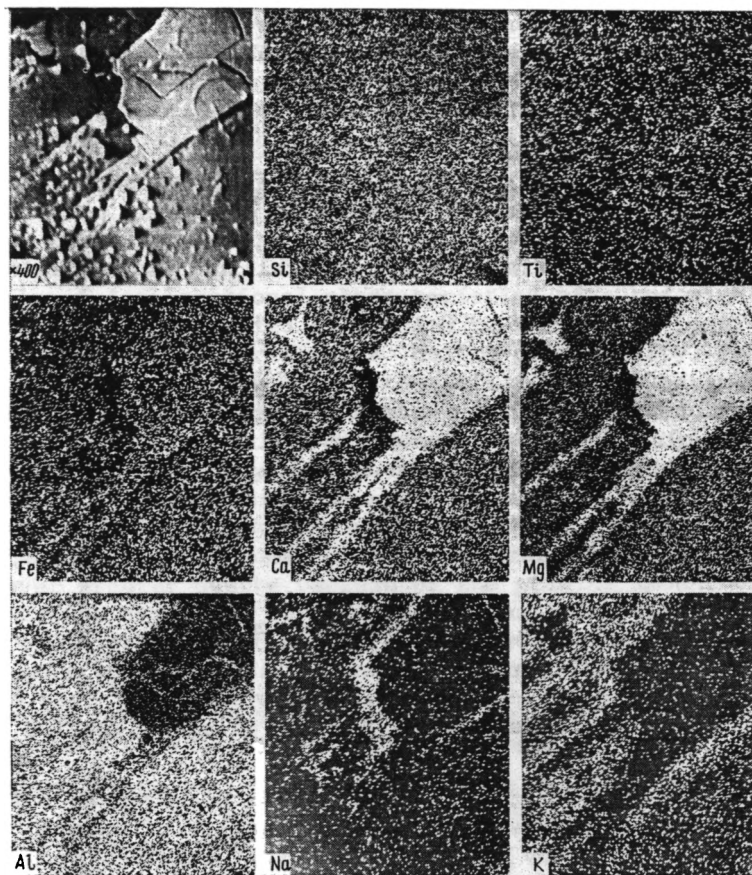


Fig. 3. Volcanic glass with a pyroxene microlite surrounded by a thin growth of acicular hornblende. Photographed in x-ray spectra of elements (by G. V. Karpova, on a Camebax x-ray spectra microanalyzer).

By microprobe analysis we also determined the quantitative composition of small crystallites, contained as an impurity inclusion in volcanic glass; in the bulk silicate analysis their presence affected the total values for some of the oxides. The following minerals were found in the crystallites: hornblende, biotite, orthoclase, and sphene (see Table 1, columns 7-11).

From the data in the table it is seen that, with increasing alteration of volcanic glass, the direction of the influx-removal of rock-forming components is revealed. It involved a decline in the content or a removal of silica, alumina, calcium, sodium, and potassium, an increase or influx and partial residual concentration of iron, magnesium, and manganese, and an influx of 8-10% water into the glass.

With the use of a microanalyzer, quantitative x-ray spectral photographs have been obtained of the various portions of volcanic glass, both without inclusions and with small crystallites of mafic minerals, orthoclase, and plagioclase. The photographs were taken in silicon, aluminum, titanium, iron, calcium, magnesium, sodium, and potassium spectra. An analysis of these results helps trace the behavior of these elements and their distribution (Fig. 3). Silicon, titanium, and (partly) aluminum are obviously unindicative. They are distributed more or less evenly over the entire area. The remaining minerals, according to their association with a particular other mineral, clearly concentrate within that mineral. Potassium and sodium behave somewhat differently. In Fig. 3 we see that sodium and especially potassium are concentrated in those portions of volcanic glass that are directly adjacent to a pyroxene crystal. We know from physics that crystallization involves release of heat. It is therefore possible that this thin portion of high-potassium or high-sodium volcanic glass on the boundary with pyroxene was also involved, after the crystallization of microcrystallites, in the process of ordering or structuring of the rock-forming components of the sili-

cate melt, but at a slightly lower temperature, at the level of secondary alteration of vitrified volcanic melt to layer silicates (smectites). The process began with the engagement of low-melting and volatile elements, such as sodium and potassium, which were among the first to respond to a change of temperature. The photographs in sodium and potassium spectra clearly reveal the qualitative distribution of these elements.

The next step in an even more detailed study of the alteration of volcanic glasses can be done by means of x-ray electron microscopy, similar to the study performed by Eggleton and Boland [8], who analyzed the weathering of minerals and their alteration to talc and smectites through a series of neomorphous transitional crystalline phases making up very thin layers (7.9 and 14 Å).

* * *

In conclusion, it should be noted that the methodology developed for detailed investigations of the alteration of volcanic glasses in Recent marine and oceanic sediments could also be used for a detailed analysis of the alteration of volcanic glasses from older sediments in folded regions. These techniques yield ample and useful information for tracing the structuring of amorphous unordered sets of volcanic glass components to anisotropic micaceous, hydromicaceous, and crystalline aggregations – such as smectites, zeolites, and possibly many other minerals.

The following conclusions have been drawn from the study:

1) the earliest secondary alterations of volcanic glass occurred more or less simultaneously with crystallization of small crystallites and microlites; they have been clearly observed in glass-microlite boundary areas in the form of palagonitization and smectitization;

2) the later stage of the alteration of volcanic glass occurred as influx and removal of isolated elements through numerous cracks that formed a perlitic texture, where palagonite, and later smectite, developed; the study has determined that calcium, sodium, potassium, silica, and aluminum were removed from volcanic glass most intensely; at the same time, an influx of water and an influx or increase in the residual concentration of iron, magnesium, or manganese were observed.

LITERATURE CITED

1. A. R. Geptner, "Palagonite and the palagonitization process," *Litol. Polezn. Iskop.*, No. 5, 113-130 (1977).
2. B. P. Zolotarev, M. N. Il'inskaya, and V. G. Korinevskii, "Composition and geochemical features of potassium alkaline variety of trachyandesitobasalt," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 1, 136-149 (1975).
3. V. G. Korinevskii, "Potassium alkaline basaltoids of the Eifelian in the Sakmarian zone of the Mugozhary," in: *Yearbook [in Russian], Inst. Geol. Geokhim. UNTs Akad. Nauk SSSR, Sverdlovsk* (1970), pp. 17-23.
4. D. I. Kudryavtsev, "Alteration of interstitial glass in effusive basalts of the Tunguska syncline," *Litol. Polezn. Iskop.*, No. 2, 139-144 (1979).
5. A. G. Kossovskaya, V. V. Petrova, and V. D. Shutov, "Mineral associations of palagonitization of oceanic basalts and extraction of metalliferous components," *Litol. Polezn. Iskop.*, No. 4, 10-31 (1982).
6. I. V. Khvorova, B. P. Gradusov, and M. N. Il'inskaya, "Hyaloclastites and their mineral alterations," *Litol. Polezn. Iskop.*, No. 3, 130-143 (1974).
7. I. V. Khvorova and B. I. Voronin, "Understanding the palagonitization process," *Litol. Polezn. Iskop.*, No. 1, 143-147 (1984).
8. R. A. Eggleton and J. N. Boland, "Weathering of enstatite to talc through a sequence of transitional phases," *Clays Clay Minerals*, 30, No. 1, 11-20 (1982).

The variations of infiltrational characteristics of a bed with increasing depth of occurrence are studied as opposed to the conventional approach of studying the permeability variations. Unlike permeability, which decreases monotonically with increasing depth, the infiltrational parameter increases with depth, attains a maximum at a certain level, and then begins to decrease. This offers better prospects for discovering and exploring commercial fluid mineral deposits at great depths than what is afforded by permeability studies.

The exploration and extraction of oil, gas, industrial, mineral, and freshwater deposits has been reaching ever greater depths because of the growing amount of mineral resources used by the economy and by the depletion of reserves at shallower levels. Another promising area involving drilling of holes to great depths is the development of geothermal power production and hydromineral chemistry [4, 7].

These developments make it important to study and evaluate the variations of the infiltrational characteristics of waterlogged beds with depth.

The current views of the variations of collector and infiltrational characteristics of rocks with increasing depths are based on a large number of theoretical and experimental studies by Soviet and foreign investigators [2, 6, 8, 10]. The results of these studies have been reviewed at the First (1977), Second (1978), and Third (1983) National Conferences convened by the interagency Lithological Committee of the USSR Academy of Sciences and Moscow Institute of Petrochemical and Gas Industry.

Among important results of these studies is the observation of a regular decrease of porosity and permeability of rocks with increasing occurrence depth. The pattern has been established with certainty for terrigenous collectors and less definitely for fissured beds, represented by carbonate rocks [2, 6, 8-10].

Despite some deviations due to lixiviation zones, faults, secondary cracking, etc., the overall reduction of bed permeability with depth is confirmed by analysis of large amounts of data and accepted by most geologists. This reduces the prospects of discovering and effectively extracting fluid deposits from greater depths and indicates a deterioration of conditions for processes involving the backpumping of water into a bed (to maintain bed pressure in oil extraction, build underground circulation systems in geothermal production, bury industrial effluents and groundwater to conserve the environment, etc.).

The permeability of rocks according to infiltration laws largely determines the value of a fluid mineral deposit. Taking into account the reduction of rock permeability with depth is essential in developing the methods for prediction and evaluation of the prospects of deposits at great depths.

According to its physical meaning based on the Darcy equation, the permeability coefficient describes only the rock's capacity for percolating liquid, but does not reflect the property of the second component of the infiltration process: the liquid itself. If we study only the collector properties in terms of permeability, the resulting description will be one-sided and insufficient for characterizing the percolation processes and their change with depth, because permeability does not fully describe these processes, which are determined by the combination of the properties of the rocks and the fluid [1, 3].

In fact, infiltrational conditions rather than collector properties (permeability per se) determine the activeness of bed systems in terms of the movement of liquid. For a given

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permeability the infiltration rate and the productiveness of a bed and a well would vary depending on the viscosity of the percolating liquid. The above-cited studies, however, were never concerned with the combined effect of the properties of rocks permeability, and the bed liquids (viscosity) as they affect infiltration depending on the occurrence depth of the natural infiltrational systems. If this combined action is considered, a different regularity of the variation of infiltrational properties of bed systems can be formulated [1]: for an infiltrational bed system consisting of a porous medium and a fluid saturating it, given a certain regional geothermal gradient and with all other conditions being equal, the infiltrational properties will increase with depth to a certain constant depth (called the optimal depth), where they will reach a maximum level; further down, these properties will decline and the rate of decrease at any depth will be slower than the rate of decrease of permeability. Any natural infiltrational system gradually subsiding in space will form at a certain depth an optimal belt with best infiltrational conditions.

This regularity is based on the following generally acknowledged principles: 1) the permeability of rocks, with other conditions being equal, decreases with depth; 2) the temperature of rocks, with other conditions being equal, increases with depth; and 3) the viscosity of fluids, with other conditions being equal, decreases with increasing temperature.

These principles, obviously, are not tied to any regional specifics and are global. This regularity of the variation of infiltrational characteristics of bed systems with depth must also be global. Since it follows from the above principles, this regularity is no less certain than these principles themselves.

It can be supported by calculation and analysis of a function $\Phi(H)$ characterizing the variation of the infiltrational properties of a fluid-saturated system with increasing bed occurrence depth H [1].

For the function $\Phi(H)$ we take the following relation, which is a complex coefficient in the Darcy equation and is described in the special literature by the term mobility:

$$\Phi(H) = K(H)/\mu(H), \quad (1)$$

where $K(H)$ and $\mu(H)$ are the variation of the permeability K and viscosity μ as a function of the depth H , respectively.

Preliminary estimates show that due to a minor variation of the specific weight of stratal waters γ as a function of depth (compared with the parameter K/μ) we do not have to operate with the more complex function — the infiltration coefficient $k = K\gamma/\mu$.

The function $K(H)$, as noted before, is one of the main variables describing the collection or properties of bed systems [2, 6, 8-10]. Numerous laboratory studies simulating bed conditions and thermobaric environments at great depths have described the variation of the permeability K with increasing depth with a sufficient certainty. It is difficult to represent this relationship by a general mathematical formula, although an attempt to this end has been made in [6]; this is because of the innumerable diversity of natural bed systems and their lithologic and petrographic properties, the various inhomogeneities, and a multitude of parameters and other factors that, in general, affect the permeability K . The author of [6] notes the largely conventional and qualitative nature of the formula and its inapplicability to practical quantitative calculations. For a theoretical proof of the regularity, however, we rely only on the main property of the function $K(H)$, namely the fact that it is a decreasing function. This property cannot be doubted because of the well-known laws of compaction of rocks with increasing pressure. The decrease, as indicated by analysis of the physical nature and the empiric relationships of the function $K(H)$ [2, 8, 9], occurs with different rates and follows different patterns in different regions and lithologic-petrographic complexes.

For water, the function $\mu(H)$ can be obtained by simultaneous solution of equations expressing viscosity as a function of the temperature $\mu(T)$ and the temperature of rocks as a function of the depth H . These equations are empiric and based on laboratory and bore hole measurements.

The function $\mu(H)$ is also a decreasing function; the rate of decrease slows down with increasing temperature and depth. For fresh water, the function $\mu(H)$ is strict, but with increasing amount of mineral content of the water the curves of $\mu(T)$ and $\mu(H)$ become shifted toward a higher viscosity.

TABLE 1

Collector properties	Geothermal gradient, Γ , °C/km		
	25	30	40
High	0.88 1260	1.07 1390	1.32 1690
Medium	0.98 409	1.17 455	1.43 555
Low	1.17 107	1.36 120	1.64 148

Note. In this and the next table, the first value is H_{opt} , the second value ϕ_{max} .

TABLE 2

Collector properties	Geothermal gradient Γ , °C/km		
	25	30	40
High	4.89 5708	5.07 6859	5.39 9440
Medium	2.36 1217	2.47 1407	2.63 1810
Low	4.35 511.7	4.52 610.7	4.79 829.8

These properties of the functions $K(H)$ and $\mu(H)$ determine the properties of the complex function $\mu(H)$ for waterlogged systems, namely [1]:

1) the high rate of variation of the function $\mu(H)$ in the initial interval of depth variation (in the range of relatively low temperatures) typical for bed fluids usually causes the function $\phi(H)$ to increase in that interval;

2) the decrease of the rate of variation of the function $\mu(H)$ at great depths (in the range of relatively high temperatures) against the background of relatively high rate of decrease of the function $K(H)$ causes the function $\phi(H)$ to decrease at these depths; and

3) the transition of the continuous function $\phi(H)$ from the rise in the initial interval to a decrease in the end interval means that there is a maximum of that function at a point of transition at a certain optimal depth H_{opt} .

A mathematical formulation of these conditions that could be used to derive further quantitative relationships is written as follows.

1. The condition of an increase of the function $\phi(H)$ in the interval $H < H_{opt}$

$$\frac{\partial}{\partial H} \Phi(H) > 0, \text{ or } \mu(H) \frac{\partial}{\partial H} K(H) - K(H) \frac{\partial}{\partial H} \mu(H) > 0. \quad (2)$$

2. The condition of a decrease of the function $\phi(H)$ in the interval $H > H_{opt}$

$$\frac{\partial}{\partial H} \Phi(H) < 0, \text{ or } \mu(H) \frac{\partial}{\partial H} K(H) - K(H) \frac{\partial}{\partial H} \mu(H) < 0. \quad (3)$$

3. The condition of the maximum of the function $\phi(H)$ at the depth $H = H_{opt}$ and for the definition of H_{opt}

$$\frac{\partial}{\partial H} \Phi(H) = 0, \text{ or } \mu(H) \frac{\partial}{\partial H} K(H) - K(H) \frac{\partial}{\partial H} \mu(H) = 0. \quad (4)$$

In the study of the infiltration of groundwater, the influence of mineral content and dissolved gas on viscosity was disregarded because it is small compared with the influence of temperature. If needed, it can be taken into account with the use of laboratory data.

Considering the dependency of the deep temperature on the geothermal gradient Γ and the temperature of the neutral layer T_0 and assuming that these values are constant for a given region, we can write a one-valued expression for the function $\mu(H)$.

In first approximation we assume that the depth dependence of the temperature $T(H) = T_0 + \Gamma H$ is linear (if the data are available, nonlinear relationships could be used); we assume the following temperature dependency of water viscosity [4, 5]:

$$\mu(T) = \frac{1744 - 1.8T}{759 + 47.7T}. \quad (5)$$

We have

$$\mu(T) = \frac{1744 - 1.8(T_0 + \Gamma H)}{759 + 47.7(T_0 + \Gamma H)}. \quad (6)$$

The function $K(H)$, as mentioned earlier, can be obtained by laboratory measurements of

rock permeabilities on specimens collected from the same stratigraphic complex in a given region at different depths. Curves of $K(H)$ plotted from such measurements [2, 6, 8, 9] exhibit a wide variety of these relationships, which can be approximated by polynomials of the first and second degree, an exponential function, etc.

For example, approximating $K(H)$ by a first-degree polynomial, we have

$$K(H) = a - bH, \quad (7)$$

where a and b are regional coefficients.

Solving (4) for H_{opt} in this case (for a linear relationship between K and H), we have

$$H_{opt} = \frac{969 - T_0}{\Gamma} - 31,4 \sqrt{\frac{1}{\Gamma} \left(\frac{969 - T_0}{\Gamma} - \frac{a}{b} \right)}. \quad (8)$$

The function $K(H)$ can be approximated by an exponential function. Then,

$$K(H) = \exp(c - mH), \quad (9)$$

$$\Phi(H) = \frac{759 + 47,7(T_0 + \Gamma H)}{1744 - 1,8(T_0 + \Gamma H)} \exp(c - mH), \quad (10)$$

where c and m are regional coefficients.

Writing (4) for approximation (9) and solving the equation for H , we obtain an equation for defining H_{opt} :

$$H_{opt} = \frac{492,4 - T_0}{\Gamma} - 5,64 \sqrt{\frac{1}{\Gamma} \left(-\frac{8109 - T_0}{\Gamma} - \frac{31}{m} \right)}. \quad (11)$$

The formulas for H_{opt} can be derived for any other definition of $K(H)$. When equation (4) cannot be solved explicitly for H , a solution can be constructed on a computer graphically, etc.

This analysis indicates that the interval above the optimal depth ($H < H_{opt}$) is one where the infiltrational properties increase with depth, while beneath the optimal depth ($H > H_{opt}$) the infiltrational properties deteriorate monotonically.

We will now describe examples of an application of these statements of the optimal depth and the belts of maximum infiltrational properties in the specific regions and lithologic-stratigraphic complexes.

According to [2], the dependence of the permeability of the Miocene rocks of the Apsheron Peninsula on the occurrence depth (i.e., the function $K(H)$) can be approximated by an experimental relation (9) with the following parameters: a) in the zone of high collector properties of rocks $c = 7.313$, $m = 0.54$; b) in the zone of medium collector properties $c = 6.16$, $m = 0.513$; and c) in the zone with relatively low collector properties $c = 4.77$, $m = 0.47$.

Taking T_0 at 10°C , a linear temperature variation with depth $T = T_0 + \Gamma H$, and considering the cases of Γ equal to 25, 30, and 40°C/km , we can calculate with formula (11) the

TABLE 3

$H, \text{ km}$	Ural-Volga region				Apsheron region			
	$K(H)$	$\frac{K(H)}{K(0,1)}$	$\Phi(H)$	$\frac{\Phi(H)}{\Phi(0,1)}$	$K(H)$	$\frac{K(H)}{K(0,1)}$	$\Phi(H)$	$\frac{\Phi(H)}{\Phi(0,1)}$
0,1	2366	1,0	1825	1,0	450	1,0	360	1,00
0,3	—	—	—	—	406	0,902	395	1,09
0,5	2270	0,959	2536	1,39	366	0,813	421	1,17
0,8	—	—	—	—	314	0,70	444	1,23
1,0	2150	0,908	3365	1,84	293	0,63	451	1,25
1,2	—	—	—	—	256	0,57	455	1,27
1,4	—	—	—	—	231	0,513	453	1,26
2,0	1910	0,807	4775	2,62	170	0,38	430	1,19
3,0	1670	0,705	5840	3,20	102	0,23	359	1,0
4,0	1430	0,604	6530	3,58	61	0,13	280	0,78
5,0	1190	0,503	6800	3,72	31	0,08	210	0,58
7,0	710	0,30	5916	3,24	13	0,029	109	0,302

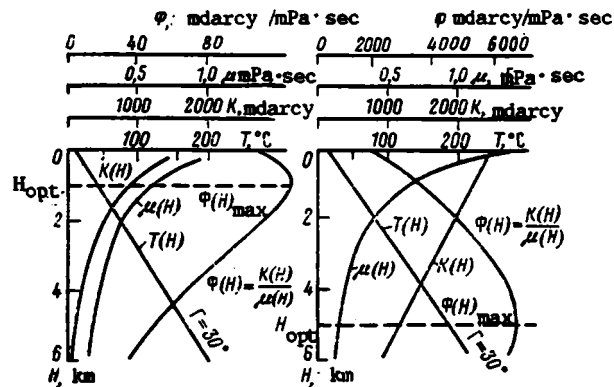


Fig. 1. Variation of permeability K , temperature T , viscosity μ , and infiltration characteristic ϕ of waterlogged beds as a function of the depth H for Apsheron (a) and Ural-Volga (b).

values of H_{opt} for all these conditions.

The results of calculations of H_{opt} and $\phi_{max}(H)$ are given in Table 1.

Figure 1a shows the cumulative curves of the depth variation of the functions $T(H)$, $K(H)$, $\mu(H)$, and $\phi(H)$ for this region.

As an example of a linear relationship between the bed permeability and the occurrence depth, we can take the results of the studies of $K(H)$ obtained by Smirnova and Yakushev [9] in the Ural-Volga region. The authors plotted graphics that are approximated well by (7) with the following parameters: a) in the zone with high collector properties of rocks $a = 2390$, $b = 240$; b) in the zone with medium collector properties $a = 852.6$, $b = 155$; and c) in the zone with relatively low collector properties $a = 235$, $b = 26$.

The values of H_{opt} and ϕ_{max} computed with (8) for the same Γ and T_0 as in the Apsheron region are given in Table 2.

The cumulative curves of the variations of $T(H)$, $K(H)$, $\mu(H)$, and $\phi(H)$ as a function of depth for this region are given in Fig. 1b.

Table 3 gives the estimates of the variations of $K(H)$ and $\phi(H)$ relative to these parameters at a depth of 100 m (where with a sufficient accuracy margin the rock temperature and the stratal water temperature are not exposed to seasonal fluctuations), i.e., the values of $K(H)/K(0, 1)$ and $\phi(H)/\phi(0, 1)$ for both these regions.

A review of the tables and curves suggests several important principles confirming the regularities of the variations of infiltration characteristics of waterlogged beds as a function of depth formulated above. The infiltration characteristics of waterlogged systems ϕ increase with occurrence depth of the bed (while the permeability K decreases monotonically), attain at a certain depth the maximum value, and then begin to decline; this is confirmed by the curves plotted on the basis of factual data (see Fig. 1). The depth at which the infiltration parameter ϕ attains its maximum depends on the type of function $K(H)$, the geothermal gradient of the region Γ , and (slightly) the temperature of the neutral layer. Depending on these values, H_{opt} can vary in a fairly broad range. For example, in one of these regions (Apsheron) H_{opt} varies from 1 to 1.5 km, while in the other (Ural-Volga) from 4 to 5 km. This means that the infiltration parameter ϕ in the latter case increases monotonically in the depth interval $H = 0-5$ km. In turn, according to the Darcy law, the predicted productive resource prospects in this range increase simultaneously and, generally, the prospects for commercial exploitation of all types of groundwater in the hydrogeological complexes of these regions improve in parallel, with all the other conditions being equal. In this region the commercial reserves of groundwater, defined ultimately as the total flow rate of all wells [7], increase almost proportionally to the growth of the parameter $\phi(H)$ (see Table 3), which in this case increases from 1825 at a depth of 0.1 km to 6800 at a depth of 5 km.

If the commercial groundwater resources are projected from variation of the infiltration characteristics with depth, these resources are thus seen to increase in the region by (6800:1825) 3.7 times, whereas if we use for the same purpose the regular decrease of

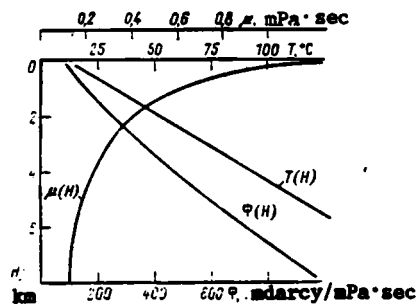


Fig. 2

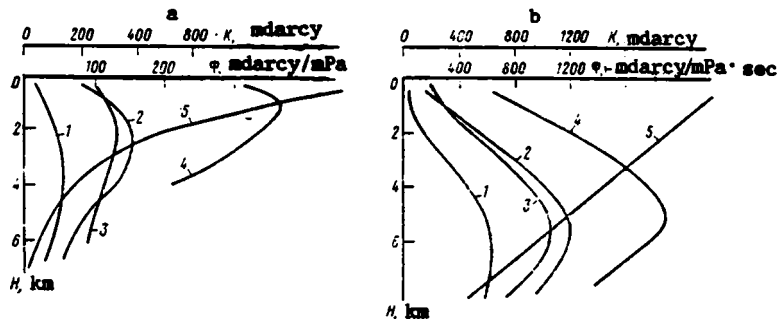


Fig. 3

Fig. 2. Variation of the infiltrational parameter ϕ for $K = \text{const} = 0.1 \cdot 10^{-12} \text{ m}^2$.

Fig. 3. Collector and infiltrational properties of oil-saturated systems as a function of depth for Apsheron region (a) and Ural-Volga region (b): 1, 2) $\mu_0 = 500 \text{ mPa} \cdot \text{sec}$ (1 - at $G = 50 \text{ m}^3/\text{m}^3$, 2 - at $G = 150 \text{ m}^3/\text{m}^3$); 3, 4) $\mu_0 = 50 \text{ mPa} \cdot \text{sec}$ (3 - at $G = 50 \text{ m}^3/\text{m}^3$, 4 - at $G = 150 \text{ m}^3/\text{m}^3$); 5) the function $K(H)$.

permeability with depth the reserve estimate would be decreased by (2366:1190), or about 2 times.

In the Apsheron region, where the depth dependency of permeability is different, the respective figures (see Table 3) are: the increase of the parameter $\phi(H)$ at the optimal depth compared with its value at 0.1 km is by a factor 1.27, while the reduction of permeability in the same interval is by a factor of 0.57.

These tables and curves also indicate that the infiltrational parameter ϕ for several kilometers is greater than its value at a depth of 0.1 km. In the Apsheron region, for example, it remains larger (than it is at the depth of 0.1 km) in the span from 0.1 to 3 km. In the Ural-Volga region the interval where ϕ is higher than at a depth of 0.1 km is 9.7 km. The permeability in these intervals in both examples, though, declines with depth and remains lower than at $H = 0.1 \text{ km}$.

A new theory adopted by several investigators is interesting: they believe that the collector properties (including permeability) in a given region are not affected substantially by the depth of the bed [10].

If that is so, we have $K(H) = K = \text{const}$, and the infiltrational parameter ϕ is merely a function of viscosity variation with depth, i.e.,

$$\Phi(H) = \frac{K}{\mu(H)}, \quad (12)$$

which means that there is a monotonic increase of the infiltrational properties of the bed as a function of depth throughout the interval from 0 to any H . The estimates of infiltrational characteristics of a waterlogged bed as a function of depth for that case of $K = \text{const} = 0.1 \cdot 10^{-12} \text{ m}^2$ are given in Table 4 and Fig. 2.

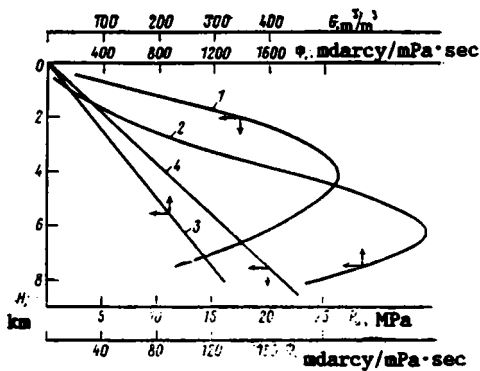


Fig. 4. Collector and infiltrational properties of oil-saturated systems as a function of depth for $G(H) = 40$ ($H \neq \text{const}$) in Apsheron and Ural-Volga regions: (1, 2) the functions $\Phi(H)$ for Apsheron and Ural-Volga regions, respectively; (3) the function $G(H)$; (4) the function $P(H)$.

TABLE 4

Parameters	Depth H, km						
	0,1	0,5	1	2	4	6	8
T , °C	13	25	40	70	100	130	160
μ (H)	1,25	0,87	0,63	39	0,32	0,14	0,102
Φ (H)	80,2	115	159	253	461	700	980

The depth curves of the temperature and water viscosity variation are also presented here. The results suggest that infiltrational characteristics of a waterlogged bed increase with depth despite constant permeability as a function of $1/\mu(H)$, and at a great depth ϕ can be several times as high as near the day surface.

A study of the infiltrational properties of oil-saturated rocks as a function of depth should take into account the discrete and random distribution of oil deposits both in plan and in depth. The question is compounded by a large number of various types of oil and the different temperature variations of their viscosity. Strictly, for each type of crude there is a separate function linking viscosity with temperature $\mu(T)$ and depth $\mu(H)$.

To study the variation patterns of the infiltrational properties of the oil-rock system as a function of depth, we will consider four types of crude with different viscosities, amounts of dissolved gas, and temperature variations of viscosity. We assume that the viscosities of these oils in a degassed state are 500 and 50 mPa·sec, and the gas factor in one case is 50 and in the other 150 m^3/m^3 .

By using the familiar methods from [5] and the thermobaric characteristics of a region, we can calculate the viscosities of these types of crude at the various depths similar to the estimates for waterlogged beds ($\Gamma = 30^\circ\text{C}/\text{km}$). Viscosity calculations at the formation temperature were performed with the formula

$$\lg \mu(T) = \frac{\lg \mu(T_0)}{1 + a(T - T_0) \lg \mu(T_0)} - \lg c, \quad (13)$$

where $\mu(T)$ is oil viscosity at the temperature T , mPa·sec; $\mu(T_0)$ is the known oil viscosity at T_0 (normally at the standard temperature of degassed oil), mPa·sec; T is the temperature at which the oil viscosity is calculated (in our case defined by the expression $T_0 + \Gamma H$), °C; and a and c are constants which reflect the oil viscosity and are taken from [5]. Oil viscosity in the bed μ_b , taking into account the amount of dissolved gas, the saturation pressure, and the formation pressure, has also been computed with this method. We assume that the formation pressure is hydrostatic and the saturation pressure is 10 MPa (in view of the lesser effect of saturation upon μ_b and in order to reduce calculations we assume one value of saturation pressure). The estimates of μ_b for the four types of crude depending on occurrence depth of the bed (i.e., the values of the functions $\mu(H)$) are given in Table 5.

The example in which the gas factor and the saturation pressure P_H are independent of the occurrence depth of the oil deposit and are constant is, strictly speaking, incorrect. Although we lack data to evaluate reliably the dependency between the amount of dissolved gas and the saturation pressure and the deposit depth, experience and practice with oil exploration indicate that the gas factor and the saturation pressure generally increase with depth. Accordingly we will consider an additional example assuming the following depth relationships of the gas and saturation pressure of oil: $G(H) = 40H$, $P_H(H) = 3H$.

TABLE 5

H, km	$\mu_0 = 500 \text{ mPa} \cdot \text{sec}$		$\mu_0 = 50 \text{ mPa} \cdot \text{sec}$	
	$G = 50 \text{ m}^3/\text{m}^3$	$G = 150 \text{ m}^3/\text{m}^3$	$G = 50 \text{ m}^3/\text{m}^3$	$G = 150 \text{ m}^3/\text{m}^3$
0,5	59,0	12,4	11,1	3,44
1	31,7	7,2	7,4	2,40
2	11,6	3,4	3,85	1,51
3	5,2	2,0	2,40	1,05
4	3,0	1,32	1,53	0,8
5	2,01	1,05	1,0	0,61
6	1,47	0,73	0,92	0,546
7	1,13	0,64	0,76	0,475

TABLE 6

H, km	$G(H), \text{m}^3/\text{m}^3$	P_H, MPa	$\mu_b, \text{MPa} \cdot \text{sec}$
0,5	20	1,5	41,3
1,0	40	3,0	14,48
2,0	80	6,0	3,57
3,0	120	9,0	1,56
4,0	160	12,0	0,824
5,0	200	15,0	0,515
6,0	240	18,0	0,350
7,0	280	21,0	0,290
8,0	320	24,0	0,243
9,0	360	27,0	0,209

These relations agree with the actual data on gas factors in oil deposits. In this example the viscosity of degassed oil μ_0 is assumed to be 100 mPa·sec. Calculations of μ_b as a function of depth for this case with the same method and all other conditions being equal, as in previous examples [5], are compiled in Table 6.

Based on functions $K(H)$ and the data of Tables 5 and 6, we have calculated for the Apsheron and Ural-Volga regions the infiltration parameter of the oil-rock system as a function of occurrence depth of the oil deposit (i.e., the parameter $\phi(H)$). Based on these estimates composite curves were plotted (Fig. 3). Only the case "a" of the functions $K(H)$ was considered.

The curves indicate that the regularity established for waterlogged beds is also valid for oil deposits at various depths. As mentioned earlier, however, each type of crude has its own function $\phi(H)$. A monotonic rise of infiltrational characteristic ϕ up to a certain $\phi_{\max}$ corresponding to $H = H_{\text{opt}}$ (despite the decline of permeability in that interval) is also observed here, followed by a decline of the characteristic.

The position of the belt of maximum infiltration properties depends not only on $K(H)$ and $\mu(H)$ but also on the gas factor G and its depth variation. In the case of oil-saturated rocks the formation pressure and the crude type (viscosity in degassed state) also play an important part; the saturation pressure is also a (less important) factor. Depending on these values H_{opt} can vary in a fairly broad interval.

In one of our examples (Apsheron) H_{opt} for low-viscosity oils varies within 1-2 km. For high-viscosity oils the maximum infiltrational characteristic zone corresponds to a depth of 3-4 km. For oil with viscosity of 100 mPa·sec (in degassed state), if the gas variation with depth is taken into account, H_{opt} for the Apsheron region is equal to 4 km.

The oil-saturated beds of the Ural-Volga region are characterized by H_{opt} equal to 4-5 km; for high-viscosity oils it is as large as 6.5 km. The belt of maximum infiltrational properties, if the gas factor depth dependency is taken into account, is also estimated to be at that depth.

In these intervals (in the range from 0 to H_{opt}) we thus observe an increase of the infiltration parameter ϕ , accompanied by an improved bed productivity, flow rate of oil wells, and the economic characteristics of a deposit. All these indicators (see Fig. 3) begin to decline only after the depth H_{opt} ; relative to their values near the present day surface a deterioration begins at an even greater depth.

The curves based on factual data thus confirm the above assertions to the effect that the infiltrational properties of bed systems (as opposed to permeability) remain higher than

TABLE 7

H, km	Aspheron region		Ural-Volga region	
	$\Phi(H)$	C_f	$\Phi(H)$	C_f
0,1	360	0,766	1825	0,268
0,5	421	0,896	1536	0,373
1	451	0,959	3365	0,495
2	430	0,915	4775	0,702
3	359	0,764	5840	0,859
4	280	0,596	6530	0,960
5	211	0,447	6800	1,00
6	152	0,323	6843	0,977
7	101	0,232	5916	0,870

their values near the present day surface for many kilometers.

Of a great practical as well as theoretical importance is the degree of increase of the parameter Φ in the zone of maximum infiltrational properties. An analysis of the curves indicates that the degree of increase as compared with Φ near the present day surface varies depending on the regional geological conditions, the characteristics of the fluid, and the amount of dissolved gas.

For the oil deposits (in Apsheron) at $\mu_0 = 500 \text{ mPa}\cdot\text{sec}$ the values of $\Phi(H_{\text{opt}})/\Phi(0.5)$ depending on the amount of dissolved gas and the collector properties of rocks range from 1.2 to 2.8. It is incorrect to analyze the infiltrational characteristics of an oil deposit at $H = 0.1$.

A study of the curves of $\Phi(H)$ for the Ural-Volga region has shown that the rate of increase of the infiltrational characteristics there is much faster than in the Apsheron region. For $\mu_0 = 500 \text{ mPa}\cdot\text{sec}$ the value of $\Phi(H_{\text{opt}})/\Phi(0.5)$ is 12-15 (at $G = 50 \text{ mPa}\cdot\text{sec}$) and 6 (at $G = 150 \text{ m}^3/\text{m}^3$), while for $\mu_0 = 50 \text{ mPa}\cdot\text{sec}$ the values are 5.5-6 (at $G = 50 \text{ m}^3/\text{m}^3$) and 2.7 (at $G = 150 \text{ m}^3/\text{m}^3$), respectively.

For a more realistic statement of the problem where $G \neq \text{const}$ but varies linearly as a function of depth, Φ , increases most in the zone of maximum infiltration characteristics (Fig. 4). For this example in Apsheron the value of $\Phi(H_{\text{opt}})/\Phi(0.5)$ is 7; in Ural-Volga it is as high as 50. At a depth of 6 km the infiltrational characteristics for this type of oil in the Ural-Volga region is thus 50 times as high as at 0.5 km (while the permeability at 6 km is 2.3 times lower than at a depth of 0.5 km).

The discrete and random distribution of oil deposits in the geological space and the collector beds and the diversity of the types of oil mentioned previously indicate that the correspondence between the real coordinates of such deposits and the calculated optimal infiltration belt based on the known functions $K(H)$ and $\mu(H)$ for a given "oil-collector" pair is random and cannot be controlled or observed exactly in nature.

Oil deposits in the sedimentary bed occur at random with respect to the depth and to the stroke as compared with the conditional belt of maximum infiltration corresponding to them. Some of them can occur near or even inside such belts, while others will be at a substantial distance from them. In the former case the deposits are in most favorable natural geological conditions in terms of their infiltrational properties that can at all exist for a given "oil-collector" pair; in the latter case the deposits are in unfavorable or less favorable conditions in terms of the infiltrational properties and thus in terms of the productivity of wells and convenience of commercial exploitation.

It is interesting to estimate the natural stratal systems and deposits in regard to their proximity or distance from the belts of maximum infiltrational characteristics. A special coefficient can be introduced to evaluate this relationship as an expression, linking the infiltrational characteristics at the bed occurrence depth with the maximum conditions for a given "fluid-rock" pair. This coefficient, C_f , called the coefficient of conditional displacement of an infiltrational system, is measured as

$$C_f = \frac{\Phi(H)}{\Phi_{\text{max}}(H)} = \frac{K\mu(H_{\text{opt}})}{\mu K(H_{\text{opt}})}, \quad (14)$$

where K and μ are the rock permeability and the fluid viscosity in the bed or the deposit

for which C_f is calculated. The coefficient C_f can be defined for a particular bed or oil deposit if we know $K(H)$ and $\mu(H)$, (the latter is known almost always for waterlogged beds). On the basis of these values we can evaluate H_{opt} and ϕ_{max} . The values of K and μ or the composite ϕ for a particular bed or deposit uncovered by drilling and being developed for exploitation are always known as a result of hydrodynamic studies of wells and sampling of oil. The theoretical coefficient C_f should vary from 0 to 1.

For waterlogged beds and oil deposits C_f can be evaluated if we know the variation pattern of permeability $K(H)$ used to estimate H_{opt} and ϕ_{max} appearing in (14). The variation of viscosity with depth $\mu(H)$ for waterlogged beds, as mentioned, is defined unambiguously, and if the geothermal gradient Γ is known can be found, in particular, with formulas (5) and (6).

The coefficient C_f at the various depths in the Apsheron and Ural-Volga regions calculated with (14) for waterlogged beds is given in Table 7. For an oil deposit $\phi(H)$ can be estimated from known oil viscosity at two different temperatures based on laboratory investigations [5].

Many of the oil deposits have low C_f . This is particularly true of high-viscosity oil deposits recently discovered in Eastern Siberia and other parts of the USSR. Some of the Apsheron Peninsula deposits are in more favorable conditions with respect to C_f (thanks to the high collector properties of beds and low oil viscosities), as well as the Grozny, Dagestan, and Stavropol regions (due to substantial occurrence depths).

The regularity of the variation of infiltrational characteristics of fluid-saturated systems, as the regular pattern of variation of collector permeability as a function of depth is therefore a general global phenomenon. Unlike the latter, this new regularity predetermines a substantial increase of the main productive characteristics and commercial criteria and generally the prospects for discovery and exploitation of commercial deposits of bed fluids at great depths. Like with depth variations of permeability, deviations from some of the basic principles may be observed for this new regularity as well. Thus, for a very high variation rate of permeability in the initial depth interval, the zone of maximum infiltrational properties can be placed conditionally above the present day surface ($H_{opt} < 0$). In that case, however, the second component of the new regularity remains in force, which states that the rate of decrease of the infiltrational characteristics with depth is much slower than the rate of permeability reduction. A situation is possible where the bed would not reach in its sinking the depth where $H = H_{opt}$. In that case, the bed will only be characterized by an increase of the infiltrational characteristics with depth. These partial deviations of the regular variation patterns of infiltrational characteristics are not ruled out theoretically, but no such instances have been observed in the analysis of available factual data.

These regularities are more definitive and rigorously established for terrigenous collectors, which is also true for depth variation of permeability.

When the depth variation pattern of permeability is disrupted, as indicated earlier (as a result of tectonogenesis, lixiviation, or cracking) [8, 10], the effect of the increase of infiltrational characteristics due to the depth reduction of viscosity is observed in the case as well.

Generally, these new regularities change drastically the current views of the prediction, discovery prospects, and exploitation possibilities of fluid deposits at greater depths.

LITERATURE CITED

1. Kh. I. Amirkhanov, G. M. Gaidarov, and M. K. Kurbanov, "Variation patterns of infiltrational properties of natural systems as a function of depth," Dokl. Akad. Nauk SSSR, 287, No. 1, 194-197 (1986).
2. L. A. Buryakovskii and R. D. Dzhevanshir, "Simulation of collector properties and cover at large depths," in: Oil and Gas Collectors at Great Depths [in Russian], MINKhiGP, Moscow (1980).
3. G. M. Gaidarov, "Infiltrational processes as a function of the thermic properties of rocks," Tr. Inst. Geol. Dag. Fil. Akad. Nauk SSSR, No. 25, 153-157 (1982).
4. A. G. Gadzhiev, V. V. Suetnov, S. A. Kasparov, et al., Problems of Geothermal Power Production in Dagestan [in Russian], Nedra, Moscow (1980).

5. Sh. K. Gimatudinov, Yu. P. Borisov, M. D. Rozenberg, et al., A Handbook of Deposit Development Planning: Design of Deposit Development Plans [in Russian], Nedra, Moscow (1983).
6. V. M. Dobrynin, Deformations and Alterations of the Physical Properties of Oil and Gas Collector Rocks [in Russian], Nedra, Moscow (1970).
7. Principles of Hydrogeology, Vols. I-VI [in Russian], Nauka, Novosibirsk (1980-85).
8. B. K. Proshlyakov, "Main stages in the exploration and the current objectives in the study of oil and gas collectors at great depths," in: Oil and Gas Collectors at Great Depths [in Russian], MINKhGP, Moscow (1980).
9. N. V. Smirnova and V. P. Yakushev, Properties of Sand Collectors at Great Depths [in Russian], Nauka, Moscow (1969).
10. V. N. Kholodov, "Formation of secondary porosity in sand collectors of ellisional basins," in: Collector Properties of Rocks at Great Depths [in Russian], Nauka, Moscow (1985).

COMPARATIVE MEASUREMENTS OF C_{org} and CO_2 CONTENTS
OF CARBONATES WITH VARIOUS METHODS

N. P. Betelev and B. I. Kudachkin

UDC 543.2

Several years ago we proposed a method for measuring C_{org} in silt and rock by annealing in an oxygen flow at 500°C for Co_3O_4 as catalyst [2, 3]. The catalyst provided for complete oxidation of the organic matter of a specimen at 500°C. Without a catalyst the oxidation was incomplete. The difference in the results of annealing with and without a catalyst is particularly dramatic when the organic matter content is high, such as in peat or anthracite [2]. The analyses can be performed on a GOU-1 gas analyzer and an AN-7529 carbon rapid analyzer (Fig. 1), as well as CHN analyzers and microanalysis equipment of various types. C_{org} content is determined by the amount of CO_2 formed in the oxidation of the organic matter of a specimen. The temperature of 500°C instead of 1000°C in the conventional method (without catalyst) eliminates the need for a preliminary removal of carbonate from the specimen, because at 500°C the common natural carbonates (calcite and dolomite) do not decay and release CO_2 . Experiments with annealing in oxygen flow showed that calcite and dolomite ground to powder begin to decay at temperatures above 500°C (calcite at 635°C; dolomite at 575°C). At 500°C neither calcite nor dolomite decay even when annealing is continued for 5 h. Siderite $FeCO_3$, magnesite $MgCO_3$, and rhodochrosite $MnCO_3$ interfere with the use of this method, because the decomposition of these carbonates and the release of CO_2 in an oxygen flow begins at 390°C. Rhodochrosite, however, is relatively rare in sedimentary rocks; it occurs in small quantities (up to 1%) and cannot affect the results of analysis significantly. Magnesite is also scarce in sedimentary rocks and present in small amounts (up to 1%); in Recent sediments any significant content of this mineral is reported only in solonchaks [5]. Literary data suggest that the total content of $FeCO_3$, $MgCO_3$, and $MnCO_3$ (with the predominance of siderite) in rocks of various geneses does not usually exceed 3% and mostly is less [3]. The presence of siderite in Recent marine sediments is believed to be unlikely [7, 8]. Where siderite is present in large amounts it forms lenses, nodules, and concretions [4] that can easily be removed from the specimens taken for analysis.

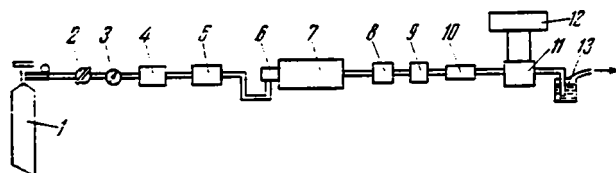


Fig. 1. Scheme of fast carbon analyzer AN-7529: 1) oxygen tank with reducer; 2) value regulating oxygen feed; 3) reducer-filter controlling oxygen pressure; 4) oxygen purification unit; 5) oxygen flow rate meters; 6) gate of annealing tube; 7) furnace for specimen annealing (the controlled furnace temperature is measured by a thermocouple); 8) filter cleansing gas of mechanical impurities; 9) vessel with anhydrous calcium chloride or anhydron for gas desiccation; 10) pipe filled with hydroperite to absorb sulfur oxides; 11) colometric calibration unit (sensor); 12) measurement unit; 13) water gate.

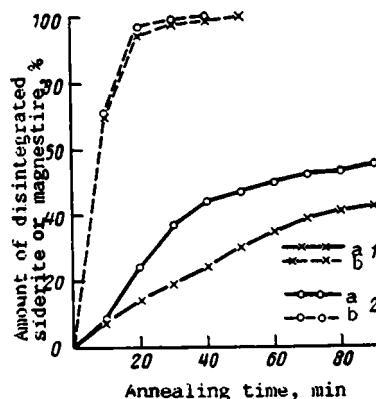


Fig. 2. Magnesite and siderite decomposition rate during annealing in an oxygen flow: (1) magnesite decomposition course at 500°C (a) and at 1000°C (b); (2) same for siderite at 500°C (a) and at 1000°C (b).

In order to evaluate the influence of a siderite or magnesite impurity on the results of determination of C_{org} content, we have studied the rate of decay of these carbonates ground to powder and annealed in an oxygen flow (Fig. 2). Within the time used for analysis by a GOU-1 instrument (maximum of 15-20 min) at most 15% of magnesite and 15% of siderite is decomposed. During the analysis with an AN-7529 analyzer (5-8 min) at most 7-8% of siderite and magnesite is decomposed (Fig. 2). In view of a minor content of carbon in siderite (10%) and magnesite (14%) and the insignificant (up to 3-5%) content of these carbonates in a scattered form in rocks, the error in the determination of C_{org} due to siderite and magnesite impurities should be small. In order to estimate the actual values of these errors we analyzed with different methods two groups of artificial mixtures consisting of powdered siderite from the Bakal deposit up to 10% and magnesite from the Satka deposit up to 7%, and also natural specimens containing up to 5% siderite (Table 1). The experiment showed that the presence of siderite impurity affected C_{org} estimates insignificantly (C_{org} in specimen 306 was 5.26%; in the same specimen with an addition of 10% of siderite it was 5.32%; the error in estimation of C_{org} due to the admixture of siderite was 1 rel.%). In natural specimens containing up to 5% siderite it did not introduce any significant error into the determination of C_{org} . This is indicated by the similarity of C_{org} determinations with our method and other analysis methods (Table 1, specimens 404, 999, and 1209).

The influence of a magnesite impurity on the estimate of C_{org} was studied in specimens with low C_{org} content (~0.3%; Table 1, specimen 950) and in specimens with a substantial amount of C_{org} (5%; Table 1, specimen 306). When 1% magnesite was added to the specimen with a small content of C_{org} the error of determination was about 20 rel.%, which is admissible for a low C_{org} (C_{org} in specimen 950 was 0.26%; after addition of 1% magnesite it rose to 0.31%). The addition of 1% magnesite to the specimen with a high C_{org} produced a negligibly small error of determination (C_{org} in specimen 306 was 5.32%; after addition of 1% magnesite it rose to 5.38%; the error determination of C_{org} due to the magnesite impurity was ~1 rel.%). The insignificance of the error in C_{org} estimates due to the presence of siderite and magnesite impurity when conducting analysis with the GOU-1 instrument has been described in [3].

Annealing in an oxygen flow at 500°C with catalyst Co_3O_4 makes it possible to determine the contents of CO_2 of carbonates as well as C_{org} . For this purpose we used the second stage of specimen annealing at 1100°C, a temperature which decomposes all natural carbonates (with release of CO_2) [9]. Tables 1 and 2 give the results of determination of CO_2 contents of carbonates of natural specimens and artificial mixes obtained with different methods. In the analysis of natural specimens of rocks a satisfactory match of CO_2 estimates by annealing at 1100°C and by Knopf's method was observed (Table 2). In the silt analysis CO_2 of carbonates determined by annealing was lower than the estimates obtained with Knopf's method (Table 1, specimen 306). The discrepancy is apparently due to the inaccuracy of analysis with Knopf's method. In the first stage of analysis with this method (boiling the specimen in 10% sulfuric acid to determine CO_2 of the carbonates), a portion of little-metamorphosed organic matter of the silt may become oxidized, resulting in a higher value of CO_2 of carbonates and a lower C_{org} of organic matter in the final data as compared with the true values. The possibility of this inaccuracy with Knopf's method is confirmed by the fact that C_{org} in the silt specimens by Tyurin's method was closer to the values obtained by annealing without decarbonization than to the results by Knopf's method (Table 1, specimen 306).

TABLE 1. Average Content of C_{org} and CO_2 of Carbonates in Specimens with Siderite and Magnesite Admixtures, Determined by Various Methods: % per Air-Dry Specimen

Specimen number	Composition	Insoluble residue, %	Knopf's method		Annealing in oxygen flow in the AN-7529 instrument with five time repetition (Institute of Oil Exploration Geology)						Oxidimetric method (Tyurin, Foundation Design Institute)
			C _{org}	CO ₂ of carbonates	with CO ₃ O _w catalyst without preliminary carbonate removal				at 1100°C with preliminary carbonate removal (annealing time 2-3 min)		
					at 500°C (annealing time 5-8 min)		annealing at 1100°C (for 3-4 min)				
					C _{org}		CO ₂ carbonate		C _{org}		
					$\bar{x}$	V	$\bar{x}$	V	$\bar{x}$	V	
404	Argillite, with 5% siderite	79,2	1,51	0,28	1,90	0,053	0,55	0,026	1,90	0,026	1,90
999	Same, with 2% siderite	88,1	0,26	3,00	0,63	0,068	2,74	0,040	0,35	0,108	0,52
1209	Same, with 1% siderite	84,6	1,57	0,34	1,90	0,007	0,55	0,013	1,74	0,014	1,93
306	Ooze from Dnieper-Bug liman	65,2	4,74	1,58	5,26	0,009	1,00	0,170	3,17	0,004	5,12
	with addition of 1% siderite	68,6	4,82	2,00	5,27	0,013	1,19	0,153	3,41	0,006	5,56
	» 2% »	63,4	4,58	1,73	5,28	0,009	1,05	0,085	3,06	0,007	5,08
	» 3% »	67,7	4,71	2,16	5,29	0,008	1,25	0,199	3,37	0,008	5,82
	» 10% »	59,1	4,36	5,04	5,32	0,019	2,51	0,074	2,74	0,011	5,34
950	Marlstone	34,2	0,27	7,74	0,26	0,054	7,48	0,017	0,18	0,044	0,43
	with addition of 1% magnesite	32,6	0,25	8,04	0,31	0,045	7,62	0,006	0,17	0,000	0,36
	» 2% »	32,5	0,24	8,22	0,39	0,078	7,86	0,006	0,16	0,000	0,41
	» 3% »	34,1	0,19	8,26	0,53	0,026	8,05	0,005	0,18	0,103	0,41
	» 5% »	32,5	0,27	8,98	0,72	0,040	8,46	0,003	0,16	0,000	0,39
	» 7% »	33,3	0,20	9,68	0,88	0,023	8,87	0,006	0,19	0,089	0,37
306	Ooze from Dnieper-Bug liman	78,6	4,41	1,48	5,32	0,004	1,12	0,047	3,30	0,026	5,26
	with addition of 1% magnesite	79,5	4,59	1,82	5,38	0,006	1,03	0,019	3,52	0,016	5,17
	» 2% »	79,6	4,40	2,78	5,39	0,002	1,30	0,019	3,50	0,021	5,20
	» 3% »	79,4	4,40	2,62	5,43	0,002	1,50	0,021	3,49	0,007	5,19
	» 5% »	75,4	4,37	3,70	5,60	0,002	1,38	0,039	3,24	0,021	4,97
	» 7% »	75,7	4,11	4,26	5,60	0,003	1,56	0,026	3,31	0,012	4,87

Note. Specimens 404, 950, 999, and 1209 are Paleozoic rocks; specimen 306 is ooze. In this and the following table, $\bar{x}$ is mean arithmetic content; V is the variation coefficient.

TABLE 2. Mean Content of C_{org} and CO_2 of Carbonates in Paleozoic Rocks Determined by Various Methods, % per Air-Dry Specimen

Specimen number	Rock	Insoluble residue, %	Knopf's method		Annealing on oxygen flow (three times)								CHN analyser (Institute of Fertilizer and Soil Science) measured by rate of release of CO ₂ [6]		Oxidimetric method (Ivurin, Foundation Design Institute)
			C _{org}	CO ₂ of carbonates	at 500°C with CO ₃ O ₄ as catalyst without preliminary carbonate removal and GOU-1 instrument		AN-7529 instrument (Institute of Oil Exploration Geology)				at 1100°C with preliminary carbonate removal (annealing time 2-3 min)				
					with CO ₃ O ₄ catalyst without preliminary carbonate removal		at 500°C (annealing time 5-8 min)		annealing at 1100°C (for 3-4 min)						
					C _{org}		C _{org}		CO ₂ of carbonates		C _{org}				
					$\bar{x}$	v	$\bar{x}$	v	$\bar{x}$	v	$\bar{x}$	v			
8	Coal	—	57,37	0,24	55,10	0,008	57,88	0,025	0,99	0,091	54,76	0,032	58,39	0,00	—
286	Limestone	1,8	0,20	41,96	0,06	0,170	0,11	0,445	43,96	0,045	0,07	0,000	0,00	42,60	0,02
287	„	12,9	0,20	38,72	0,21	0,080	0,18	0,222	37,84	0,049	0,18	0,333	0,00	37,20	0,24
294	„	2,8	0,24	43,40	0,22	0,205	0,18	0,194	43,63	0,040	0,12	0,167	0,00	42,90	0,15
402	Sandstone	86,5	1,21	0,38	1,30	0,046	1,42	0,041	0,37	0,189	1,20	0,200	1,22	0,77	1,26
409	Clay	83,6	4,33	0,00	4,88	0,021	4,50	0,032	0,37	0,135	4,86	0,136	4,49	0,66	4,03
410	Coal	72,5	26,27	0,10	25,00	0,016	27,87	0,046	0,73	0,068	21,27	0,081	28,24	0,00	—
412	Siltstone	84,4	0,31	0,00	0,40	0,050	0,42	0,057	0,29	0,206	0,45	0,067	0,32	0,22	0,87
657	Clay	78,3	1,06	0,82	1,45	0,000	1,59	0,065	0,70	0,071	1,11	0,027	1,35	0,59	0,98
1110	Limestone	14,2	0,87	35,68	0,01	0,143	0,76	0,075	38,14	0,033	0,47	0,532	0,97	35,00	1,02

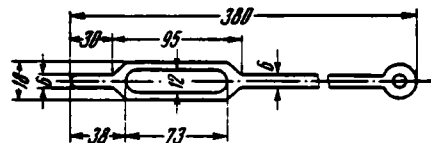


Fig. 3. Frame for insertion of vessel into annealing tube of the AN-7529 instrument.

An important merit of annealing at 500°C with catalyst Co_3O_4 compared with the conventional annealing at about 1000°C is the elimination of the labor-consuming preliminary removal of carbonates from the specimen, which takes up about half of the work in the analysis. In addition, the decarbonization with an acid alters and destroys some of the organic material of the specimen. The loss of organic matter is particularly great in case of its low degree of metamorphism, as in Recent sediments. This is illustrated by analysis of ooze from a Dnieper-Bug liman (Table 1, specimen 306), where C_{org} by annealing at 500°C with Co_3O_4 catalyst without decarbonization was on average 5.29%. Similar results were obtained with Tyurin's method (5.19%) and Knopf's method (4.58%). When the same specimen was investigated with the standard procedure by annealing at 1100°C preceded by decarbonization (boiling in 10% HCl, followed by flushing of acid), the C_{org} estimate was 3.24%. The loss of C_{org} to acid decarbonization of Recent ooze was about 40%.

Lowering the temperature from 1000-1100 to 500°C results in a more than double saving of electricity, prolongs the service life of equipment, and makes analysis safer, preventing the risk of ignition of high-organic specimens when placed in the annealing chamber. Ignition is dangerous and distorts the results of analysis because it causes a loss of a portion of the CO_2 .

The cobalt oxide catalyst Co_3O_4 produced by Soviet industry is not toxic, is readily available, and has no noxious side effects. Besides intensifying oxidation, cobalt oxide also absorbs some of the sulfur oxides formed by annealing [1], facilitating the purification of gas after combustion and prolonging the service life of gas analyzer absorbers. The catalyst costs about 20 rubles/kg (a single analysis takes up at most 1 g). The catalyst is taken in an amount of approximately 30 times the weight of the organic matter of the specimen and carefully mixed with the specimen, ground to powder in the annealing chamber.

The performance of the AN-7529 rapid carbon analyzer is about twice as high as that based on Knopf's method. The annealing time in the first stage (at 500°C) is 5-8 min; in the second stage (at 1100°C) it is 3-4 min. The action of the rapid analyzer is based on determining by colometric titration the amount of CO_2 released from the specimen as a result of heating. The carbon content is displayed on the instrument indicator, adjusted for the specimen weight. To recalculate the readings to CO_2 content, the carbon content of carbonates displayed on the AN-7529 indicator during the second stage of heating should be multiplied by the coefficient 3.66. This coefficient has been calculated on the basis of atomic weight of carbon and oxygen in the CO_2 molecule. An analysis of specimens by annealing in two steps should be conducted in batches, switching the furnace to the respective temperature conditions. Containers with specimens between the first and second annealing stages should be stored in an exsiccator. The standard set of absorbers of the AN-7529 unit should be supplemented by a vessel with anhydrous calcium chloride or anhydron for gas dessication (see Fig. 1-9). At 500°C the annealing tube in the instrument remains dark; for convenience of placing the vessel in the annealing tube a special frame should be used which is made of a heat-resistant low-carbon sheet steel about 2 mm thick. The frame for standard porcelain containers is 80 mm long and 13 mm wide. It is shown in Fig. 3.

For C_{org} estimates the specimen weight should be from 0.4-0.3 g at low (1-3%) content of C_{org} to 0.05-0.02 g at high (30-100%) content. The weight of the specimen for evaluation of CO_2 of carbonates is 0.2-0.4 g, depending on the carbonate content.

The analyses were performed with a GOU-1 instrument; the variation coefficient of C_{org} content was on average 0.074 (Table 2). The accuracy of measurement on the scale of the gas measurement burette of the GOU-1 instrument was approximately 0.15% for a content of 5% of C_{org} in the sample and a weight of 0.15 g. With increasing specimen weight the accuracy of measurements was improved. In analysis with the AN-7529 the variation of C_{org} determination was on average 0.056; for carbonate CO_2 it was 0.063 (Tables 1 and 2). According to the specification certificate of the AN-7529 instrument, the error of measurements with specimens containing up to 1.5% of carbon is not more than 0.01%, and in analysis of specimens containing up to 4% of carbon not more than 0.05%. Practical tests show that the AN-7529 can be used for carbon measurements even at a higher content (up to 100%).

LITERATURE CITED

1. S. M. Atashyan and A. A. Abramyan, "Cobalt protoxide-oxide as a catalyst in sulfur oxide combustion and absorption," *Arm. Khim. Zh.*, 24, No. 8, 673-676 (1971).
2. N. P. Betelev, "A new method for measuring organic matter in soils and rocks," *Inzh. Geol.*, No. 2, 105-110 (1979).
3. N. P. Betelev, "Measuring organic carbon content in silts and rocks by specimen annealing in an oxygen flow without preliminary carbonate elimination," *Litol. Polezn. Iskop.*, No. 5, 152-159 (1981).
4. G. I. Bushinskii, "Conditions of accumulation of siderites, vivianites, and brown pyrites in Byelorussian swamps," *Byull. MOIP, Otd. Geol.*, 21(3), 65-80 (1946).
5. D. M. Kuguchkov, "Mineralogic composition of salinized soils in Zeravshan Valley," *Tr. Uzbeksk. s.-kh. Inst.*, 13, 8-14 (1970).
6. R. A. Srapenyants, E. S. Brodskii, K. N. Klyagin, and L. K. Shevtsova, "Rapid measurements of carbon content in soil by the combustion method," *Argokhimiya*, No. 7, 138-143 (1979).
7. M. F. Stashchuk, *Redox Potential in Geology* [in Russian], Nedra, Moscow (1968), pp. 154-175.
8. N. M. Strakhov, *Principles of the Lithogenetic Theory*, Vol. 2 [in Russian], Izd-vo Akad. Nauk SSSR, Moscow (1960), pp. 501-511.
9. A. I. Tsvetkov, E. P. Val'yashikhina, and G. O. Piloyan, *Differential Thermal Analysis of Carbonate Minerals* [in Russian], Nauka, Moscow (1964).

OBITUARY

GEORGII FEDOROVICH ROZHKOVA

Georgii Fedorovich Rozhkov, Doctor of Geological and Mineralogical Sciences, Chairman of the Department of Lithology, and Collectors of the VNIIGRI, died suddenly on October 1, 1986.

G. F. Rozhkov was born November 15, 1927. He survived the Blockade of Leningrad and there, 15 years old, started his professional career. In 1947-1948 G. F. Rozhkov worked as a collector at VNIIGRI, and served in the Army. After graduating from the Mining Institute in 1958, G. F. Rozhkov worked at VNIIGRI, where he advanced from collector to Chairman of the department.

G. F. Rozhkov was a petroleum geologist who had surveyed different regions of the country from Central Asia to Timan. He made a great contribution to the development of the theory and methods of fractional granulometric analysis. He improved the method of analysis, wrote new computer programs for statistic data processing, and proposed a fundamentally new dynamogenic diagram. G. F. Rozhkov combined his theoretical and methodical researches to the solution of practical problems of petroleum geology, such as surveying of zones of the thinning out of the collectors and traps of the nonanticlinal type oil and gas in the terrigenous precipitates. His candidate dissertation (1967) was devoted to the surveying of the zones of the thinning out of the granular collectors in the deposits of the Lower Cretaceous at Tadzhik depression. His doctoral dissertation, defended in 1980, was entitled "Granulometry in the surveying of the lithological traps of oil and gas."

G. F. Rozhkov and his associates started integrating lithologic-paleogeographic and geophysical, basically seismic, research for surveying of the nonanticlinal traps in as terrigenous deposits. His development of this problem was honored with the Medal of Exhibition of Soviet National Economic Achievements. During the last years of his life, G. F. Rozhkov conducted field works in the Timano-Pechorsk province, where his method of integrating the lithologic-geophysical research for surveying of the nonanticlinal traps in Paleozoic deposits was tested. His recommendations in the direction of the drilling of deep wells in this region were adopted by industrial organizations.

G. F. Rozhkov authored over 100 scientific works. A wide circle of specialists, from petroleum geologists and engineers to seismologists, consulted with him. All of them received not only comprehensive responses, but also careful and helpful attention from him. G. F. Rozhkov lectured to the aspirants of UNESCO in the Mining Institute.

A great scientist full of creativity has passed away. The bright memory of his dynamic personality and scientific achievements will forever remain in the hearts of his co-workers and all who knew him.

Editorial Board of *Litologiya i Poleznye Iskopaemye*

All-Union Petroleum Scientific-Research Institute of Geoprospecting (VNIIGRI). Translated from *Litologiya i Poleznye Iskopaemye*, No. 1, p. 141, January-February, 1988.

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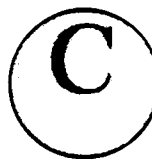
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